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Eastern Environmental Radiation Facility Radiochemistry Procedures Manual

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This manual provides a convenient and accurate reference for the determination of pertinent radionuclides and stable elements in environmental and bioassay samples. All of the described procedures have been used routinely in the analysis of many samples.

In addition to the chemical procedures, sections have also been included on radioactivity counting, standardization, and quality control. Periodically, the manual will be updated and corrected with new procedures and sections added.

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EASTERN ENVIRONMENTAL RADIATION FACILITY

RADIOCHEMISTRY PROCEDURES MANUAL

Compiled and Edited by
Robert Lieberman

June 1984

U.S. Environmental Protection Agency
Office of Radiation Programs

Eastern Environmental Radiation Facility
P.O. Box 3009
Montgomery, AL 36193

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FOREWORD

The Eastern Environmental Radiation Facility (EERF) in Montgomery, Alabama, is a field laboratory operated by the Office of Radiation Programs of the United States Environmental Protection Agency. Prior to December 2, 1970, the EERF was known as the Southeastern Radiological Health Laboratory and operated by the United States Public Health Service. This manual is the first publication of radiochemical procedures used at the EERF since the 1965 publication by the Public Health Service of Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples (Public Health Service Publication No. 999-RH-10). Due to the time elapsed since last publication and the EERF's changes in direction since its incorporation into the Environmental Protection Agency, a comprehensive manual of analytical procedures used is overdue. Beyond documentation, our purpose in publishing the manual is to provide a means of exchanging information with other laboratories and with other individuals, groups, and organizations working with the Environmental Protection Agency.

Although other procedures exist for some of the analyses addressed in this manual, those procedures that we have chosen to publish are those that we know to be most appropriate and effective for ambient and environmental levels and, generally, for our needs here at the EERF. All of the procedures in the manual have been exposed to rigorous intra- and interlaboratory analytical quality control, and we have strong confidence in the results that will be obtained using them. Many of the procedures have been published elsewhere and we make no claim to originality regarding them. However, we have tried to write and present the procedures clearly in order to make them useable by the greatest number of technically competent persons. Finally, by way of assurance, all those procedures included in this manual that are associated with EPA standards requiring analysis of radionuclides are certified EPA alternate procedures.

The manual reflects the careful efforts of many people over nearly twenty years of work. I would like to acknowledge all of their contributions. Robert Lieberman deserves special recognition for his labor over a long period of time in assembling these procedures and working toward an accurate and consistent presentation of them.

Especially since the material in this manual will be periodically updated, we would like to invite and encourage comments, suggestions, and discussion of the procedures. Remarks should be addressed to the Director, Eastern Environmental Radiation Facility, P. O. Box 3009, Montgomery, Alabama, 36193.

Charles R Porter

Charles R. Porter, Director
Eastern Environmental Radiation Facility

Montgomery, Alabama
June 1984

PREFACE

This manual provides a convenient and accurate reference for the determination of pertinent radionuclides and stable elements in environmental and bioassay samples. All of the described procedures have been used routinely in the analysis of many samples. In addition to the chemical procedures, sections have also been included on radioactivity counting, standardization, and quality control.

Periodically, the manual will be updated and corrected with new procedures and sections added. The page numbering system, which is similar to that of the HASL-300 Procedures Manual, has this end in mind. Each division in this manual has been given a letter. The first pair of digits with each letter represents sections of a division and the last pair of numbers is the pages within the section. In Division C on Chemical Procedures, the element symbol precedes any numbers, the first pair of numbers is the specific procedure for that element, and the second pair is used for the page number. Thus, C-Am-01-01 is page 1 of the first procedure for americium.

Certain sequential and multielement analyses will be found at the end of the division under C-00-01, etc.

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QUALITY ASSURANCE PROGRAM

Introduction

The quality assurance program is a separate entity at the Eastern Environmental Radiation Facility (EERF), removed organizationally from the functional groups it serves, the Monitoring and Analytical Services Branch and the Environmental Studies Branch. The main purpose of the EERF quality assurance program is to establish limits of acceptable radioanalytical results and to assure that analytical results stay within these error limits. When analytical results deviate from established limits, appropriate laboratory personnel determine the cause and take immediate remedial action. The need for a quality assurance program is underscored by the fact that established limits are not fixed. They change as new technologies and procedures develop.

Program Functions and Responsibilities

Preparation of Standard Radioactive Sources and Solutions

Quality assurance personnel, coordinating with counting room personnel, stock appropriate radioactive standards and prepare the standards in various counting geometries for instrument calibration. The primary source of radioactive standards is the Environmental Protection Agency (EPA) National Quality Assurance Program at the Environmental Monitoring and Support Laboratory, Las Vegas, Nevada (EMSL-LV). Other sources include the National Bureau of Standards (NBS) and commercial suppliers of certified standards. Table 1 describes the standards required for each type of radioassay and the minimum frequency of each calibration. Table 2 lists the nominal radioactivities for these calibration standards.

Counting room personnel calibrate the instruments and perform the stability checks, and quality assurance personnel verify the results of the checks for specified performance. The Environmental Studies Branch calibrates and maintains the field measurement and sampling equipment, and quality assurance personnel supply the appropriate standards as required. (Table 3 lists the types of field equipment used at the EERF and their calibration frequencies.) In addition, quality assurance personnel prepare solutions containing known quantities of various radioisotopes as needed by analytical personnel to validate or modify radiochemical procedures.

Intrafacility Cross-Check Program

Four types of samples are analyzed in the EERF cross-check analysis program. Routinely, every tenth sample through the laboratory is analyzed in duplicate. In addition, each week a 'spiked' sample and a 'blind' sample are analyzed. A spiked sample is one which has not been previously analyzed and which has had added to it a measured quantity of at least one radioisotope that is routinely analyzed at the laboratory. A blind sample is a sample of material that has been previously analyzed but whose identity is unknown by the analyst at the time of reanalysis. Finally, the cross-check program includes periodic analyses of samples to determine background levels of radioisotopes. Table 4 outlines the intrafacility cross-check program. The Computer Services Section maintains all data generated from this program in the central data repository.

Interlaboratory Cross-Check Program

Quality assurance personnel participate in three interlaboratory programs. The first and most comprehensive program is the EPA National Quality Assurance Program at the Environmental Monitoring and Support Laboratory, Las Vegas, Nevada (EMSL-LV). Tables 5 and 6 describe the EMSL-Las Vegas cross-check program. Table 5 lists the available cross-check samples, and Table 6 shows the distribution schedule. "Environmental Radioactivity Laboratory Intercomparison Studies Program", 1978-1979, (EPA 600/473-032) describes this program in further detail.

The second interlaboratory program in which EERF quality assurance personnel participate is the intercomparison analysis studies conducted by the World Health Organization (WHO) and the International Atomic Energy Agency (IAEA). Participation in these studies is limited to the analytical disciplines represented at the EERF. During the year, the EERF receives four or five samples consisting of specific radioisotopes in various materials.

Finally, the EERF participates in periodic intercomparison analysis studies. These studies are usually brief and involve specific radioisotopes in a particular sample medium. Such analyses are usually done by specific request to the EERF. Requests originate from other government agencies and, on occasion, from professionals in the private sector.

In addition to the above three programs, the EERF, on an as-needed basis, utilizes reference materials made available by other agencies. The NBS, WHO, IAEA, and EMLS-LV, for example, often make reference materials available. EERF quality assurance personnel procure these materials whenever lab personnel determine a reference need.

Data Storage

The Computer Services Section stores all data pertaining to the quality assurance program. The kinds of data that are stored include the following:

-all intrafacility and interfacility comparison analyses results with related performance

-all data related to reagent blanks, instrument backgrounds, chemical recoveries, instrument counting efficiencies, and instrument calibration

-all replicate sample analyses results

Analytical Performance Review

Quality assurance personnel continuously review all data relating to the radioanalytical performance of the EERF. When they find variances from control limits, they notify supervisory personnel who review all pertinent data and procedures. If necessary, the laboratory tests procedures to identify causes for the variances. Subsequently, quality assurance personnel institute modifications, if necessary, to assure that similar variances will not recur. Every two years the EERF publishes a report that reviews and discusses results of its quality assurance program (ORP/EERF-79-2).

Support Functions By Other EERF Staff

To be successful, the quality assurance program requires the support and cooperation of personnel in other units of the laboratory. These support tasks and responsibilities, according to personnel category, include the following:

-Counting room personnel conduct daily stability checks and frequent background counts and calibrate all instruments. Proper records of these checks are maintained in the counting room.

-Analytical chemistry personnel repeat the analysis of one sample for every 10 samples analyzed (replicate analyses) and analyze at least one reagent blank for every 20 samples analyzed. They maintain the established procedure for sample identification. All radiochemical methods are used by facility personnel as they appear in the manual. Personnel conduct all radiochemical procedures as documented and modifications to the procedures are not permitted without approval by the laboratory director and notification of quality assurance personnel. Computations are monitored for accuracy by spotchecks.

-Computer services personnel periodically review the accuracy of electronically computed results, evaluate results for proper error terms, maintain the state-of-the-art methodology for analytical computations consistent with available computer capabilities, and maintain the central data repository.

References

1. Kanipe, L.G., Handbook for Analytical Quality Control and Radioanalytical Laboratories, EPA-600/7-77-088, August 1977.
2. Blanchard, R., Broadway, J. and Moore, J., The Eastern Environmental Radiation Facility's Participation in Interlaboratory and Intralaboratory Comparisons of Environmental Sample Analyses: 1979 and 1980, EPA 520/5-82-012, January 1982.

TABLE 1

Description of Required Radioassay Standards and Calibration Frequencies

	Gamma Ray Systems	Beta Particle Systems	Alpha Particle Systems	Liquid Scintillation	Radon Emanation
Standards required	standard radioisotope solutions (1-liter and 3.5-liter Marinelli beakers)	predetermined weights of strontium carbonate and yttrium oxalate precipitates with known amounts of ^{89}Sr, ^{90}Sr, and ^{90}Y	specific isotope analysis: standard solutions of $^{238-234}$U and ^{239}Pu on planchets gross alpha analysis: standard uranium solutions and self-absorption standards	radiation standards in aqueous solutions	standard ^{226}Ra solutions
Calibration frequency	annually	quarterly	monthly (for specific isotope analysis)	^{3}H (biannually) ^{222}Rn (biannually) ^{14}C (annually)	annually

NOTE: Table 2 lists the nominal radioactivities for calibration standards.

TABLE 2

Nominal Activities of Radionuclide Standards for Gamma Ray Efficiencies

	dpm/sample					
	Cylindrical NaI Crystal*			NaI Crystal	Ge(Li)	
Radioisotope	400 ml	1 liter	3.5 liter	40, 85 ml	40, 85 ml	400 ml
^{40}K	50 g KCl**	100 g KCl	200 g KCl	20 g K_2CO_3***	20 g K_2CO_3	50 g KCl
^{51}Cr	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5
^{54}Mn	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4
^{58}Co	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4
^{59}Fe	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5
^{60}Co	7×10^4	7×10^4	1×10^4	7×10^4	7×10^4	7×10^4
^{65}Zn	1×10^5	1×10^5	2×10^5	1×10^5	1×10^5	1×10^5
^{95}Zr/^{95}Nb	3×10^4	3×10^4	6×10^4	3×10^4	3×10^4	3×10^4
^{106}Ru	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5
^{110m}Ag	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4
^{124}Sb	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4
^{131}I	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5
^{134}Cs	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4

TABLE 2--Continued

Nominal Activities of Radionuclide Standards for Gamma Ray Efficiencies

	dpm/sample					
	Cylindrical NaI Crystal*			NaI Crystal	Ge(Li)	
Radioisotope	400 ml	1 liter	3.5 liter	40, 85 ml	40, 85 ml	400 ml
^{137}Cs	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4	5×10^4
$^{140}Ba/^{140}La$	3×10^4	3×10^4	3×10^4	3×10^4	3×10^4	3×10^4
$^{144}Ce/^{144}Pr$	3×10^5	3×10^5	3×10^5	3×10^5	3×10^5	3×10^5
^{226}Ra	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5	1×10^5
^{232}Th	4×10^4	4×10^4	4×10^4	4×10^4	4×10^4	4×10^4

* Crystal is 10 cm diameter and 10 cm in height.

** There are 966 dpm ^{40}K per gram of KCl that yield 106 (11 percent) 1.46 MeV photons/min.

***There are 1043 dpm ^{40}K per gram of $K_2 CO_3$ that yield 115 (11 percent) 1.46 MeV photons/min.

NOTE: Nominal activities are those that are sufficient to accumulate enough counts in a short period of time without excessive instrument dead time.

TABLE 3

Calibration of Field Equipment

Type of Equipment	Calibration Frequency
Air monitoring calibration equipment	Annually
Air pumps for ERAMS stations	Prior to shipment and annually thereafter
Thermoluminescence dosimeters (TLD's)	Annually
Pressurized ionization chambers (PIC's)	Annually

TABLE 4

Intrafacility Comparison Program

Radioisotope	Sample Media*	Analysis
Selected gamma-ray emitters	water, milk, solids	NaI, Ge(Li) or both
^{89}Sr, ^{90}Sr, or both	water, milk, solids	specific analyses or gross beta
Selected actinides	water, milk, solids	specific analyses or gross alpha
^{222}Rn	water	specific analyses
^{226}Ra	water, solids	specific analyses
^{3}H	water, milk	specific analyses
^{14}C	milk	specific analyses

* The prepared samples are rotated randomly to provide at least one intercomparison per week. These intercomparisons could either be previously analyzed samples for which contents are known or specially prepared spiked samples.

TABLE 5

Summary of EMSL-LV Cross-Check Programs

Sample	Analysis	Activity Per Isotope	Quantity Supplied	Preservative	Distribution	Time for Analysis and Report
Milk	^{89}Sr, ^{90}Sr, ^{131}I, ^{137}Cs, ^{140}Ba, K	< 200 pCi/liter	~ 4 liters	Formalin	Quarterly	6 weeks
Water						
Gross alpha beta*	Gross alpha, beta	< 100 pCi/liter	~ 4 liters	0.5M HNO_3	Bimonthly	4 weeks
Gamma	^{60}Co, ^{106}Ru, ^{134}Cs, ^{137}Cs, ^{51}Cr, ^{65}Zn	< 500 pCi/liter	~ 4 liters	0.5M HNO_3	Bimonthly	4 weeks
^{3}H	^{3}H	< 3500 pCi/liter	~ 50 ml	none	Bimonthly	4 weeks
^{239}Pu*	^{239}Pu	< 10 pCi/liter	~ 4 liters	0.5M HNO_3	Semiannually	8 weeks
Ra	^{226}Ra, ^{228}Ra	< 20 pCi/liter	~ 4 liters	0.5M HNO_3	Quarterly	8 weeks

TABLE 5--Continued

Summary of EMSL-LV Cross-Check Programs

Sample	Analysis	Activity Per Isotope	Quantity Supplied	Preservative	Distribution	Time for Analysis and Report
Sr	^{89}Sr, ^{90}Sr	< 50 pCi/liter	~ 4 liters	0.5M HNO_3	Triannually	8 weeks
Blind	Any Combination of	< 200 pCi/liter	~ 4 liters	0.5M HNO_3	Semiannually	10 weeks
Air Filter	Gross alpha beta* ^{90}Sr, ^{137}Cs	< 200 pCi/sample	3 - 5 cm. dia. air filters	none	Quarterly	6 weeks
Soil*	^{238}Pu, ^{239}Pu ^{228}Th, ^{230}Th, ^{232}Th	< 50 pCi/sample	~35 grams	none	Semiannually	8 weeks
Diet	^{89}Sr, ^{90}Sr, ^{131}I ^{137}Cs, ^{140}Ba, K	< 50 pCi/sample	2 - 4-liter samples	Formalin	Triannually	8 weeks

* Laboratories must have the necessary licenses before receiving these samples.

TABLE 6

EMSL-LV Cross-Check Sample Distribution Schedule

(Numbers indicate week of the month)

Month	Water							Milk	Food	Air Filter	Soil
	gamma	Gross alpha beta	^{3}H	^{226}Ra ^{228}Ra	^{239}Pu	^{89}Sr ^{90}Sr	Blind*	Sr gamma	Sr gamma	Gross alpha, beta, ^{137}Cs, ^{89}Sr	Pu, Th
Oct	1		2				3	4			
Nov		3							1		2**
Dec	1		2	3						4	
Jan		3			2	1		4			
Feb	1		2								
Mar		3		2					1	4	
Apr	1		2				3	4			

TABLE 6--Continued

EMSL-LV Cross-Check Sample Distribution Schedule

(Numbers indicate week of the month)

Month	Water							Milk	Food	Air Filter	Soil
	gamma	Gross alpha beta	^{3}H	^{226}Ra ^{228}Ra	^{239}Pu	^{89}Sr ^{90}Sr	Blind*	Sr gamma	Sr gamma	Gross alpha, beta, ^{137}Cs, ^{89}Sr	Pu, Th
May		3				1					2***
Jun	1		2	3						4	
Jul		3			2			4	1		
Aug	1		2								
Sep		3		2		1				4	

* Performance sample for the Water Supply Laboratory Certification Program.

** Thorium analysis only.

***Plutonium analysis only.

INSTRUMENTATION

Beta Particle Counting - Low Background

Instrumentation

The beta counters are of the low-background, multiple-detector type with one or more sample detectors per unit. Steel or lead shielding is used to attenuate external gamma radiation. Guard detectors operating in anti-coincidence with the sample detectors reduce the background contribution due to cosmic interactions. The sample detectors are gas-flow, window-type Geiger counters, approximately 5 cm in diameter. The counting gas is a mixture of 99.05 percent helium and 0.95 percent isobutane. The beta counters are equipped with preset timers. All samples are placed in 5 cm diameter stainless steel planchets for counting.

Operating Voltage

The voltage on the detector necessary for proper operation is determined by running the "plateau curve" of count rate versus high voltage. The correct operating voltage is selected in one of the following two ways:

1. The initial operating voltage.
    - A. With check source of known value in place, increasingly higher voltage is applied to the detector until it begins to count.
    - B. At the point where it begins to count, a one minute count is recorded.
    - C. The voltage is increased an integral amount that is convenient such as 20 or 50 volts.
    - D. Another one minute count is recorded.
    - E. Steps C and D are repeated until two consecutive readings are obtained that lie within the same two sigma region. The proper operating voltage is the higher voltage of these two points.

F. Eleven one minute counts are made to determine whether all counts do lie within the two sigma area.

G. If more than one count lies outside the two sigma area, the operating voltage is biased in the opposite direction of the outliers. (Lower if high and higher if low).

H. In this event the check source is recounted at the new operating voltage for eleven one minute counts to determine whether these eleven points lie within the two sigma area.

2. The monthly check of the operating voltages for detectors in operation:

A. With check source in place a one minute count is recorded.

B. The operating voltage is lowered by the normal metering increment for that instrument and another one minute count is recorded.

C. This procedure is continued until the count rate of the check source falls below the two sigma area.

D. This procedure indicates that the instrument is functioning properly and the operating voltage is then reset to the second voltage increment into the two sigma region.

E. The check of the operating voltage is completed by repeating 1Fand 1H above.

WARNING

Do not apply a voltage to a detector to make it go into a saturated discharge condition. This causes two problems: (1) the 60 gauge wire in the detector becomes oxidized, overheated, and possibly misshapen due to warping or sagging, and (2) the high voltage power supply becomes overloaded, which may damage some of its components.

The correct operating voltage should be determined at least once each month, after the gas supply is changed, after any electronic maintenance, or after any modification is made on a detector. Any appreciable change in the operating voltage, plateau length, or plateau slope indicates possible trouble in detector electronics or in the counting gas. It is desirable not to interrupt the gas flow for any reason, but, if that is not possible, as when the counting gas is changed on a counter, purge the detector for several hours before applying high voltage to the detectors and guard.

Counting Efficiency

Counting efficiency is the relationship between sample disintegration rate and sample counts recorded by the counter. Counting efficiency is usually expressed as counts per disintegration or as the percentage of disintegrations recorded as counts. Counting efficiency may also be expressed as the count rate per unit of radioactivity, i.e., cpm per pCi/l.

Counting efficiency is determined by placing a source with a known disintegration rate or known radioactivity in the beta counter and measuring its count rate. This source is referred to as a standard source, and the process of determining the counting efficiency is called calibration. Calibration should be performed for each radionuclide that will be counted in the counter, and the standard sources should be of the same physical form (size, shape, chemical composition, planchet material, etc.) as the samples to be counted. Gross beta calibration is performed using a standard source of strontium-90 plus yttrium-90 in equilibrium. The results of a gross beta determination of a sample is then reported as activity equivalent to strontium-90 plus yttrium-90 in equilibrium. (See Standardization Section for preparation of standards.)

Beta counters should be calibrated every four to six months and after mechanical modifications are made on a detector. The daily operational check procedure as outlined below serves also as a check on the relative counting efficiency.

Background Determination

The background counting rate of the low-background beta counters is usually between 0.5 and 1.5 counts per minute. It can vary from detector to detector and from day to day. The background for each detector should be determined with an overnight measurement and at the beginning of the workday for the length of time that routine samples are counted (or another specific time) and should be measured using a clean, empty planchet in each counter. Radon fluctuations in the atmosphere will affect the background count rate of the beta detector.

Absorption Factor

The beta counting efficiency is determined using an essentially weightless standard source. In many types of samples there is a sufficient amount of solids so that the sample partially shields itself and produces 'self-absorption'. In this case, the count rate obtained on the sample is not as great as it should be and must be corrected for self-absorption according to the weight, or more correctly the 'density-thickness' (mg/cm^2) of the sample.

The absorption correction factors should be determined for the specific radionuclide being counted and for approximately the same chemical composition as in the actual sample. A curve of the absorption correction factor versus sample weight or density-thickness can be obtained by preparing a sample that contains equal concentrations of radioactivity per unit weight of solids and varying amounts of solids (solids content should vary from approximately zero solids to a weight equal to the maximum weight expected in an actual sample). Be sure that the radioactivity is uniformly distributed in the solid material. The count rate per unit weight of solids for each sample is then divided by the count rate of the weightless sample, and this fraction is plotted as a function of the sample weight. It is not necessary to use a calibrated solution for this study since all values are compared to the weightless sample value.

Sample Handling

All samples should be handled with care to prevent accidental loss of the material in the planchet, contamination of the counting room, or contamination of the beta counters. All samples should be kept covered when not actually in a counter to keep dust from the samples. Samples which tend to be hygroscopic should be kept in a desiccator until counted. Planchets that have material piled above the top edge of the wall or have material on the outside of the planchet should not be placed in the beta counters. Some types of samples consist of a precipitate on a 2.5-cm diameter filter. The filter should always be in the center of the 5 cm planchet when the planchet is being placed into the counter. Care should be exercised that the filter not warp or the use of a metal ring may be necessary.

Counter Operation Check

At the beginning of each workday, a standard check source should be counted to determine that the counter is operating satisfactorily. The count obtained each day should be compared with the usual count of the check source for that particular detector. A count significantly higher or lower than the usual value indicates detector or electronic malfunction or insufficient counting-gas supply. A graph of the daily check source counts showing the acceptable limits of variation is desirable.

Sample Types and Counting Times

Table 1 gives the types of samples counted for beta activity, counting times, and general remarks pertinent to each sample type.

Alpha particle Counting - Internal Proportional Counters

Instrumentation

The alpha counters are the internal proportional gas-flow type and are operated on the alpha plateau in the proportional region. The counting gas is 'P-10', a mixture of 90 percent argon and 10 percent methane. The detectors are hemispherical with approximately 6.3 cm diameters. After insertion of each sample, the detector must be purged for approximately four minutes before the count is started.

Operating Voltage

The plateau curves for the alpha counters are obtained in the manner described in Part A above. In addition, to assure that the counter is on the alpha plateau rather than the alpha and beta plateau, a beta standard is counted in the chamber. The voltage on the detector is lowered until it counts only alpha disintegrations and the alpha plateau curve is obtained in this region.

Counting Efficiency

The standards used to determine alpha counting efficiencies should approximate the samples to be counted in physical size and backing material. Comments found in Part A apply. Natural uranium (in equilibrium) or a specific alpha emitter such as plutonium-239 may be used as the calibration source.

Background Determination

The background counting rate of the alpha counters varies from 0.03 to 0.20 count per minute, depending upon the particular counter. Each afternoon the planchet holder is cleaned and an overnight background is obtained in each counter. If the background exceeds the normal background count, the chamber is decontaminated as outlined below.

Self-Absorption Factor

Because an alpha particle is readily stopped in matter, the number reaching the sensitive volume of the detector is greatly reduced by self-absorption and scattering in the sample material. To correct for this, it is necessary to determine the self-absorption factors for alpha counting. Alpha self-absorption factors are determined in the same manner as the beta self-absorption factors. Samples are prepared containing equal concentrations of alpha radioactivity per unit weight and varying amounts of solids, and the count per unit weight is plotted as a function of the solids weight (mg) or 'density-thickness' (mg/cm^2). The samples used to determine self-absorption should resemble the actual samples as much as possible in physical size, planchet material, and chemical composition, and the alpha emitter should be the same as used to determine alpha counting efficiency.

As it is usually not practical to prepare a 'weightless' alpha sample in the laboratory, the self-absorption curve may be extrapolated to find the count rate at zero density-thickness. If a standard solution is used to prepare the self-absorption samples, the weightless sample counting efficiency is determined from the extrapolated count rate at zero density-thickness. The self-absorption factors are computed by dividing each count rate per unit weight by the extrapolated weightless sample count rate. The self-absorption factors thus computed may be plotted as a function of either total sample weight (mg) or density-thickness (mg/cm^2) to obtain the self-absorption curve.

Sample Handling

The comments as given for beta counting apply here.

Counter Operation Check

The same procedure is followed here as outlined for beta counters.

Decontamination

Because the alpha samples are placed inside the detector, an internal proportional detector may easily be contaminated. Approximately every six months, or at any time the background increases above the level normally encountered, the detector should be removed and thoroughly cleaned with ethanol. A brown film often appears on the walls of the detector. This film should be removed by lightly rubbing with an abrasive. Soap pads are routinely used at this laboratory. The manufacturer suggests the use of an abrasive (NMC proportional counter manual). The center wire should be cleaned by dipping in ethanol (with care not to bend it out of its normal shape). The accumulation of this deposit on the chamber walls leads to a gradual deterioration in performance (generally observed as an increasing operating voltage, change in plateau slope, and decreasing plateau length). A sudden deterioration in performance usually indicates mechanical damage to the center wire or an accumulation of dust or debris on the center wire.

Sample Types and Counting Times

Table 2 gives the types of samples counted for alpha activity, counting times, and general remarks pertinent to each sample type.

Gamma Ray Spectroscopy

Sample Preparation

All samples are usually gamma scanned for specific gamma ray-emitting nuclides before they are processed, i.e., they are gamma scanned in the 'raw' form as received at the laboratory. The only preparation required is to make sure the sample is homogeneous and is in calibrated configuration. For solid media it is necessary to grind and blend the sample before counting. Normally a 3.5- or 1.0-liter aliquot of the homogeneous sample is placed in a clean, polyethylene, Marinelli-type beaker and analyzed by gamma ray spectroscopy.

Instrumentation

The gamma ray spectrometer consists of a detector, multichannel pulse height analyzer, data read-out device, and auxiliary instrumentation. The detectors used here are 10 x 10 cm NaI(Tl) solid or 12.7 x 10 cm well crystals coupled to photomultiplier tubes and enclosed in steel cave-type shields. The Marinelli-type beaker containing the 3.5-liter sample is placed over the detector inside of the shield.

Calibration

Two types of calibration are required in gamma ray spectroscopy: gamma ray energy vs. channel number and gamma-counting efficiency. Knowledge of the energy-channel number relationship permits qualitative identification of specific gamma ray-emitting nuclides. In order to make a quantitative determination of the amount of a particular nuclide, it is necessary to know the counting efficiency and the shape of the standard spectrum for that nuclide.

Gamma ray energy-channel number relationship. The spectrometers are used with two energy-channel number relationships. For most of the samples from routine programs, 200 channels of an analyzer are used to cover the energy range from 0 to 2 MeV, at 10 keV per channel. The spectrometers are aligned to the proper energy-channel number relationship by counting several nuclides with gamma ray energies in the energy range of interest (0 to 2 MeV) and plotting the location (channel number) of each peak as a function of the known gamma ray energy. Varying the gain of the amplifier in the analyzer changes the slope of this line and, in effect, changes the energy-channel number relationship by a constant factor (multiplier). Increasing the gain by a factor of 2 changes the slope by a factor of 2 and changes the energy calibration by a factor of 2. Thus, a peak which initially was located in channel number 10 would now appear in channel number 20. This relationship is true only if the plot of channel number versus gamma ray energy passes through the origin (zero). The threshold control changes the X-axis intercept and permits one to adjust the spectrometer so that the line passes through the origin. Often it will be necessary to adjust the threshold, adjust the gain, readjust the threshold, readjust the gain, and so forth, to achieve perfect calibration.

Most multichannel analyzers exhibit some nonlinearity, that is, a plot of photon energy versus channel number will not result in a perfectly straight line. This is most apparent in the lower energy portion of the spectrum (< 100 keV). A procedure commonly used is to make ^{60}Co (1.332 MeV) and ^{137}Cs (0.662 MeV) fall in channels 133.2 and 66.2 by adjusting the gain and threshold controls. The other nuclides are then counted and the peak channels determined and plotted against energy. A list of nuclides used for standardization is shown in Table 3.

Gamma ray counting efficiency. The counting efficiency and spectrum shape must be determined for each of the nuclides that one desires to measure quantitatively. Counting efficiency is usually expressed in units of counts per minute in a selected spectral region per picocurie or counts per minute per picocurie per liter. A known amount of activity of a particular nuclide is diluted to the desired volume with distilled water, thoroughly mixed, placed in a Marinelli beaker, and counted. This standard solution should be counted for a sufficient length of time to obtain a total count which will yield good counting statistics. A total count (in the spectral region of interest) of approximately 10,000 counts is adequate if only the photopeak efficiency is to be determined.

Geometries in use at this laboratory are 3.5- and 1.0- liter Marinelli beakers and a 400-ml plastic container for use with the 10 x 10 cm solid crystals and 40- and 85-ml plastic vials for use with the 12.7 x 10 cm well crystal.

(3) To obtain standard spectra for the analyses of data, it is necessary to prepare samples with standards of the radionuclides of interest in the required geometries. It is desirable but not always practical to duplicate as closely as possible the sample density with the standards. These spectra should contain statistically sufficient net counts in each region of interest upon which to base the interference coefficients and photopeak efficiencies. Table 4 presents typical photopeak efficiencies for the three geometries in use at this laboratory.

Routine Counting Procedure

(1) At the beginning of each workday, small cesium-137 and cobalt-60 standards (point sources) are counted for 5 minutes in a uniform geometry. From the location of the peaks, the energy alignment of the spectrometer is checked and adjusted, if necessary. A check on counting efficiency is obtained by comparing the counts in selected spectral regions to the usual counts for these sources. A plot of these daily counts on a control chart as a function of data will indicate sudden degradation in counting efficiency as well as long-term changes in efficiency, if such should occur. Radioactive decay of the standards must, of course, be taken into consideration. This daily procedure also checks out the operation of the complete spectrometer system, including the data read-out device.

(2) After checking the energy alignment and counting efficiency of the spectrometer system, a background count is made on each detector using a sample of distilled water having the same geometry as the samples to be counted. The background should be counted for the same length of time as the samples or, preferably, longer.

If the background is to be subtracted automatically by the spectrometer, the background data should be stored in the spectrometer in the subtract mode. If background is not to be automatically subtracted, the background is stored in the add mode, printed out, and erased from analyzer memory. The background must be scrutinized to determine that it is normal and that there is no evidence of contamination of the detector or shield.

(3) The beaker containing the sample is placed in position and counted for an appropriate length of time. A 50-minute counting time is normally used.

Analysis of Spectral Data

The analysis of the spectral data obtained from the gamma ray spectrometer is an important and usually the most complicated aspect of the use of this instrument to measure radionuclide concentrations. If one is interested in only a qualitative determination of the radionuclides in a sample, i.e., identification of the gamma ray emitters, then the location of the peaks in the spectrum is of primary interest. If one desires to determine the amount of a particular nuclide in the sample, then the location of the peaks, the number of counts in the peaks, and the interference of one peak with another all must be considered. A number of methods have been used for analyzing gamma ray spectral data. Two of these methods in general use are described below. Both are suitable for use with a desk calculator.

Stripping method. In this method, the spectrum of each radionuclide is successively stripped from the composite spectrum of the sample. Beginning with the nuclide having the highest energy photopeak, the amount of this nuclide is first determined. The standard spectrum of this nuclide is then normalized to the high energy photopeak in the sample spectrum and the normalized standard spectrum is subtracted channel by channel from the sample spectrum. Having removed the spectrum of the highest energy gamma ray-emitter from the composite spectrum, the next highest gamma energy photopeak is selected, the amount of radioactivity determined, the standard spectrum for this radionuclide normalized to the sample spectrum, and the spectrum of this radionuclide stripped from the composite spectrum. This procedure is continued until all identifiable radionuclides present in the sample have been quantitized. It should be noted that the stripping method is most useful in the case when only a few gamma ray-emitting nuclides are present in the sample. Also, if there is direct interference between the photopeaks of different nuclides, the stripping method becomes somewhat inaccurate. A further disadvantage is that if a particular nuclide has more than one gamma ray, usually the highest energy gamma ray must be used as the normalizer and, in some cases, the photopeak from this gamma ray may be extremely low compared to other peaks in the spectrum. The errors associated with each successive 'strip' are cumulative, causing the error to be great in the lower energy end of the spectrum.

If only one gamma ray-emitting radionuclide is present in the sample, the amount of the radionuclide may be determined directly from the net count (gross count - background) in the selected photopeak region. The same spectral region must be used in the sample spectrum as was used in the standard spectrum when counting efficiency was determined.

If only three or four gamma ray-emitting nuclides are present in the sample and if their photopeaks are separated in energy, a simplified stripping procedure may be used. The simplified procedure consists of subtracting the Compton spectrum of higher energy gamma rays from the photopeak of the lower energy gamma rays. In most cases, the Compton spectra are approximately straight lines in the regions of the lower energy photopeaks, that is, the counts do not vary greatly from one channel to the next. Thus, a straight line is drawn across the base of the photopeaks of interest and the counts above this baseline are taken as the counts due to the nuclide of interest. This procedure is applied to a net spectrum, that is, after the background has been subtracted. The following formula describes the procedure:

$$\left(\begin{array}{c}\text{Gross counts in}\\ \text{spectral region}\\ \text{of interest}\end{array}\right) - \left(\begin{array}{c}\text{Background}\\ \text{counts}\end{array}\right) - \left(\begin{array}{c}\text{Baseline}\\ \text{counts}\end{array}\right) = \left(\begin{array}{c}\text{Counts due}\\ \text{to nuclide}\\ \text{of interest}\end{array}\right)$$

Matrix (simultaneous solution) method. The matrix method is similar to the stripping method in that the interference of the spectrum of one nuclide with that of another is considered, but the interferences are subtracted simultaneously rather than successively, as in the stripping method. Interference in regions of energy higher than the photopeak are considered as well as the interference in regions of lower energy. Cases of direct interference of photopeaks also can be handled by this method. The paper by Kahn et al. (Ref. 2) and the U.S. Public Health Service training course manual Radionuclide Analysis by Gamma Spectroscopy (Ref. 3) give a detailed discussion of this method.

In general, equations are set up describing the contribution of each radionuclide to the counts in a selected spectral region of interest. The number of equations corresponds to the number of nuclides. The contributions of each nuclide to a given spectral region are determined from the individual spectra of standard sources. The set of equations is then solved simultaneously. Such simultaneous solutions are most easily performed by a computer when the number of nuclides (and hence the number of equations) is more than two or three. The solutions of the set of equations are then new equations that give the count due to each nuclide of interest in terms of the observed counts in each spectral region and constant factors. In using these equations, the net count is determined (gross count - background) in each of the selected spectral regions of the sample spectrum, these values are inserted into the equation, and the true count due to each nuclide is computed. The counting efficiency factors are then used to obtain the amount of each radionuclide in the sample. Inaccuracy may result if a nuclide is present in the sample but is not accounted for in the set of equations.

A third method, the Least Squares Analysis, necessitates the use of a computer. This method is described in the course manual Radionuclide Analysis by Gamma Spectroscopy (Ref. 3).

Alpha Particle Scintillation Counting

Radium-226 is determined at this laboratory by the emanation technique. The procedure used to prepare and seal the sample is described in Section C of this manual. After the sealed solution has been stored for the ingrowth of ^{222}Rn, the radon is drawn by vacuum and flushed by nitrogen into a ZnS-lined scintillation cell. The counting system consists of a photomultiplier tube (which interfaces the scintillation cell), an electronic circuit which amplifies and shapes the photomultiplier signal, and an electromechanical or electronic scaler. Since the levels of radium encountered in environmental samples are very low, long counting times are necessary, on the order of 1000 minutes per sample.

The efficiency and background of each chamber is determined before use with a sample. The efficiency is determined by introducing a known amount of ^{222}Rn gas into the scintillation cell and counting until a statistically valid number is obtained. The chamber is then cleaned by alternately evacuating and purging with nitrogen. When free of all residual radon, the background of the chamber is determined by a 1000 minutes count.

The repetitive determination of backgrounds and efficiencies serves as a check on the operation of the system in lieu of the daily performance tests recommended for the previously described systems.

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5. Phillips, C.R., Stewart, J.A., and Athey, T.W. III, A Computer Program for the Analysis of Gamma-Ray Spectra by the Method of Least Squares, U.S. Department of Health, Education, and Welfare, Public Health Service Publication Number 999-RH-21 (1966).

TABLE 1

Beta Particle Counting Sample Types and Counting Times

Sample Type	Nuclide	Counting Time	Remarks
Yttrium oxalate on 2.5-cm diameter filter (milk, water, food)	^{90}Y	50 min	Place filter in center of 5 cm planchet. Count as soon as possible to reduce correction for ^{90}Y decay.
Strontium oxalate (total strontium) on 2.5-cm diameter filter (milk, water food, biota, silt and soil	^{89}Sr and ^{90}Sr	50 min	Place filter in center of 5 cm planchet. Count as soon as possible to reduce correction for ^{90}Y ingrowth and ^{89}Sr decay. Count again after 6-7 days to determine ^{90}Sr by differences.
Gross beta (5 cm) on planchet (water, food, biota, silt, and soil)	Gross beta	20-50 min, depending on count rate of sample	Handle samples carefully to avoid spilling contents.

TABLE 2

Alpha Particle Counting Sample Types and Counting Times

Sample Type	Nuclide	Counting Time	Remarks
Gross alpha (5-cm) on planchet (water, food, biota, silt, and soil)	Gross alpha	25-100 min	Handle planchet carefully to avoid spilling contents.
Total radium-barium chromate on 2.5-cm diameter filter (water, food, biota, silt, and soil)	Total radium	100 min	Place filter in center of 5 cm planchet. Count as soon as possible to avoid correction for radium daughter ingrowth.

TABLE 3

Nuclides Useful for Calibrating Spectrometer

Nuclide	Half-life*	Energy of principal gamma rays (MeV)	Channel No. 10 keV/Channel
^{57}Co	270 d	0.123	12.3
^{144}Ce	285 d	0.134	13.4
^{141}Ce	32.5 d	0.142	14.2
^{133}Ba	10.5 y	0.360	36.0
^{131}I	8.04 d	0.364 0.637	36.4 63.7
^{140}Ba-^{140}La	12.80 d	0.487 0.537 1.596	48.7 53.7 159.6
^{103}Ru-^{103}Rh	39.35 d	0.498	49.8
^{106}Ru-^{106}Rh	368 d	0.513	51.3
^{137}Cs	30.17 y	0.662	66.2
^{22}Na	2.60 y	0.510 1.277	51.0 127.7
^{54}Mn	313 d	0.840	84.0
^{65}Zn	244 d	1.119	111.9
^{60}Co	5.27 y	1.173	117.3
^{40}K	1.277×10^9	1.46	146.0

* Half-life of parent nuclide.

TABLE 4

Typical Efficiencies for a 10cm x 10cm NaI (Tl) Crystal

Radionuclide	Energy Band MeV	Photopeak Energy MeV	3.5-1	1.0-1	*Cottage Cheese Container
^{144}Ce	0.09 - 0.13	.134	0.012	0.121	0.018
^{131}I	0.33 - 0.39	.366	0.048	0.080	0.060
^{106}Ru	0.47 - 0.55	.511	0.0097	0.016	0.012
^{137}Cs	0.62 - 0.70	.662	0.034	0.057	0.038
^{95}Zr-^{95}Nb	0.71 - 0.79	.76	0.034	0.050	0.036
^{54}Mn	0.80 - 0.88	.84	0.035	0.058	0.042
^{65}Zn	1.06 - 1.18	1.11	0.015	0.027	0.017
^{60}Co	1.27 - 1.39	1.332	0.022	0.036	0.027
^{40}K	1.40 - 1.52	1.46	0.0023	0.0038	0.029
^{140}Ba	0.45 - 0.53	0.49	0.036	0.058	---
^{140}Ba-^{140}La	1.53 - 1.67	1.60	0.020	0.032	0.025
^{226}Ra-^{214}Bi	1.69 - 1.83	1.76	0.0048	0.0090	0.0068

* A round, plastic (four inch diameter) container having a 450 ml capacity.

NOTE: The efficiency is defined for preselected channels spanning the photopeak and is determined by the equation $E = \frac{\text{net cpm}}{\text{dpm in the standard}}$.

PREPARATION OF STANDARDS FOR INSTRUMENT CALIBRATION

Preparation of Strontium-90 and Yttrium-90 Secondary Standards

Principle

In most procedures for determining ^{90}Sr and ^{90}Y, yttrium is determined as the oxalate, and strontium either as the oxalate or carbonate. A known quantity of a ^{90}Sr-^{90}Y primary standard is mixed with a predetermined amount of stable strontium and yttrium carrier, and a radiochemical separation is made. Strontium can also be precipitated as nitrate in concentrated nitric acid solution, and yttrium can be precipitated as the hydroxide.

The preparation of pure standards of ^{90}Sr and ^{90}Y is of prime concern rather than a quantitative recovery; however, the yield has been generally over 95 percent. Since these standards are used for procedures which require the addition of carriers, self-absorption curves are prepared.

The amounts of strontium and yttrium carrier used in the accompanying procedures are approximately 10 mg each of yttrium and strontium. Slight changes in the amount of carrier would not change the results. Much larger amounts of carrier have been used successfully with the necessary procedural modification related to self-absorption.

Since the principal product in nitrate separation is strontium, it is used to prepare the radiostrontium standard. The principal product in the hydroxide separation is yttrium, and this is used to prepare the radioyttrium standard. Both procedures, however, are suitable for preparing both strontium and yttrium standards.

In the nitrate procedure, strontium is separated from yttrium by precipitation in a concentrated nitric acid solution. This is a separation method which has been used frequently in the past. Both strontium and yttrium nitrate carriers are used and the separation process is repeated several times to assure purity of precipitate. Although the quantitative recovery of strontium is of secondary importance, a high recovery is desirable. Strontium nitrate is insoluble in a 70 percent nitric acid solution. A 90 percent nitric acid solution permits the addition of up to 10 ml of water and, therefore, the use of carrier and standard radiostrontium solutions without the need of evaporation. Fresh nitric acid should be used. Older nitric acid solutions tend to decompose, losing some of the nitric acid content, and thus reduce recovery. The purity of strontium standard is checked by following the same nitrate precipitation procedure and replacing ^{90}Sr-^{90}Y with approximately 10 nanocuries of ^{90}Y separated from a ^{90}Sr-^{90}Y solution. Since no radiostrontium is present, any radioactivity in the strontium precipitate would indicate an impure standard.

The same technique is used to determine the purity of yttrium standard by replacing ^{90}Sr-^{90}Y with approximately 10 nanocuries of ^{85}Sr.

The hydroxide separation of strontium and yttrium is carried out employing the difference in the solubilities of their hydroxides. Both strontium and yttrium carriers are added and yttrium hydroxide is precipitated with ammonium hydroxide and purified by multiple reprecipitations. The recovery is over 95 percent.

The determination of purity in this procedure is the same as described in the nitrate separation. In both cases the impurity is less than 0.1 percent.

The precipitation of yttrium and strontium as oxalates as well as the strontium carbonate precipitation are established procedures. Strontium is precipitated as oxalate or carbonate in an ammoniacal solution by the addition of ammonium oxalate or sodium carbonate.

The precipitation, in most cases, is reasonably complete within a few minutes, if it is cooled in an ice bath. Strontium oxalate precipitates as $SrC_2O_4 \bullet H_2O$. Yttrium is precipitated as oxalate in an oxalic acid medium. As in the case of strontium oxalate, the precipitation is complete in a few minutes, if cooled in an ice bath. Yttrium oxalate precipitates as $Y_2(C_2O_4)_3 \bullet 9H_2O$.

Special Apparatus

1. Metricel DM 800 membrane filters or equivalent, 25mm diameter, 0.8 micrometer pore size. See Note 1.
2. Suction filter apparatus.
3. Centrifuge, bench model.

Reagents

1. Ammonium hydroxide, 15M. Reagent grade NH_4OH.
2. Ammonium oxalate, saturated solution. Dissolve 142 g of ammonium oxalate crystals in 500 ml of hot distilled water and dilute to 1 liter with distilled water.
3. Ethanol, 95 percent reagent.
4. Nitric acid, fuming 90 percent.
5. Nitric acid, 16M, 70 percent reagent.
6. Nitric acid, 2M. Dilute 125 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
7. Oxalic acid, 1M. Dissolve 126 grams of crystalline oxalic acid reagent in 700 ml distilled water and dilute to 1 liter.
8. Sodium carbonate, 1.5M. Dissolve 159 g of Na_2CO_3 in 900 ml distilled water and dilute to 1 liter.
9. Strontium carrier, 10 mg Sr^{+2}/ml. Dissolve 24.2 g $Sr(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16M HNO_3 and dilute to 1 liter.
10. Yttrium carrier, 10 mg Y^{+3}/ml. Heat (avoid boiling) 12.7 g of Y_2O_3 in 50 ml of 16M HNO_3 until dissolved. Transfer to a 1 liter volumetric flask and dilute to 900 ml. Adjust to pH2 with 15M NH_4OH and dilute to 1 liter with distilled water.

Procedure - Nitrate Separation

Strontium-90 Oxalate or Carbonate

1. Pipette 1 ml of strontium carrier (approximately 10 mg Sr^{+2}/ml) and 1 ml of yttrium carrier (approximately 10 mg Y^{+3}/ml) into a centrifuge tube. Add 1 ml of ^{90}Sr-^{90}Y standard activity and

dilute to approximately 10 ml with distilled water.

2. Add 30 ml of fuming nitric acid. Cool with stirring in ice bath for 10-20 minutes, centrifuge, and decant the supernate containing yttrium into a beaker. Record the time as the start of decay of yttrium.
3. Wash precipitate from step 2 with 3 ml of fuming nitric acid; centrifuge, decant, and discard the supernate.

3a. For strontium carbonate precipitate, wash precipitate from step 3 with 3 ml of fuming nitric acid, centrifuge, decant, and discard the supernate.

3b. Dissolve the precipitate in 10 ml of distilled water and add 3 ml of 15M ammonium hydroxide.

3c. Heat to near boiling in hot water bath and add 5 ml of 1.5M sodium carbonate and cool in ice bath. Go to step 6 after precipitating strontium carbonate.

4. For strontium oxalate precipitate, proceed from step 3b to step 5.
5. Heat to near boiling on hot water bath, add 5 ml of ammonium oxalate, and cool in ice bath.
6. Centrifuge, discard supernate.
7. Transfer strontium carbonate or oxalate precipitate quantitatively onto a pre-weighed membrane filter with three 10 ml portions of water and wash with three 10 ml portions of cold alcohol.
8. Carefully mount the filter in a 5 cm planchet, weigh, and count the strontium-90 activity.
9. Mount filter carefully in a 5 cm planchet and count.

Yttrium-90 Oxalate

10. Evaporate the supernate from step 2 almost to dryness.
11. Transfer the contents of the beaker quantitatively into a centrifuge tube with four 10 ml portions distilled water.
12. Add 5 ml of 15M ammonium hydroxide, stir, centrifuge, and discard supernate.

13. Dissolve the precipitate in 20 ml of 2M HNO_3.
14. Repeat steps 12 and 13.
15. Follow steps 5-9 of the Hydroxide Separation.

Procedure - Hydroxide Separation

Yttrium-90 Oxalate

1. Transfer 1 ml of yttrium carrier into a centrifuge tube and add 1 ml of strontium carrier.
2. Add 1 ml of ^{90}Sr-^{90}Y standard activity and dilute to approximately 20 ml with distilled water.
3. Add 5 ml of 15M ammonium hydroxide, stir, and centrifuge the yttrium hydroxide. Transfer the supernate into a 100 ml beaker to be used for strontium precipitate. Record the time as the start of decay of yttrium.
4. Dissolve the precipitate from step 3 in 20 ml of 2M HNO_3.
5. Add 5 ml of ammonium hydroxide, stir, and centrifuge the precipitate. Discard the supernate.
6. Repeat steps 4, 5, and 4 again.
7. To precipitate yttrium oxalate, add 5 ml of 1M oxalic acid and adjust to pH 1.5 with a pH meter, using approximately 2 ml of 15M NH_4OH. Stir and cool in an ice bath 10-20 minutes. Centrifuge and discard the supernate.

Strontium-90 Oxalate or Carbonate

8. Transfer the precipitate quantitatively onto a membrane filter with three 10 ml portions of cold water. Wash with three 10 ml portions of cold alcohol, dry, and weigh.
9. Mount filter carefully in a 5 cm planchet and count.
10. Evaporate the supernate of step 3 almost to dryness.
11. Transfer the contents of the beaker quantitatively with two 5 ml portions of distilled water and three 10 ml portions of fuming nitric acid into a centrifuge tube.

12. Cool in ice bath for 10-20 minutes, centrifuge, and discard the supernate.
13. Follow the nitrate separation procedure for strontium oxalate or carbonate precipitation procedure starting at step 3.

Yttrium-90 Efficiency Calculation

The recovery of yttrium is calculated by comparing the weight of yttrium carrier precipitated as yttrium oxalate and the weight of the sample.

The efficiency is calculated by means of

$$E = \frac{C}{(A)(R)(D)},$$

where

E = counting efficiency of yttrium cpm/dpm,
T 1/2 = the half-life of yttrium-90 (64.2 hours),
t = time lapse from precipitation to counting (hours),
C = net counts per minute,
A = original activity in dpm,
R = radiochemical yield express as recovery of yttrium, and
D = the decay calculated from $D = e - \frac{.693\ t}{T\ 1/2}$.

Sample Calculation

Sample Number	C	A	R	t	D
1	251	507	0.96	2.25	0.976
2	249	510	0.95	2.50	0.973

$$E_y = \frac{251}{(0.96)\ (507)\ (0.976)} = 0.52$$

$$E_y = \frac{249}{(0.95)\ (507)\ (0.973)} = 0.53$$

Strontium-90 Efficiency Calculation

The recovery of strontium is determined by comparing weight of strontium carrier and that of precipitate on the filter.

Calculate the strontium-90 efficiency using the following equation:

$$\text{Efficiency} = \frac{A-[(B)(C)(D)(E)]}{(B)(C)} = \frac{A}{(B)(C)} - (D)(E)$$

where

A = net counts per minute,

B = original activity in dpm,

C = radiochemical yield expressed as recovery of strontium carrier,

D = the efficiency of the counter for ^{90}Y,

E = ingrowth of ^{90}Y calculated from $1 - e^{\frac{-.693}{T}t}$,

t = time from ^{90}Y separation to counting (hours), and

T = the half-life of yttrium.

Sample Calculation

Sample Number	A	B	C	t	E	D
1	267.7	800	0.98	12	0.122	0.52
2	272.3	800	0.97	12	0.122	0.52

$$E_{Sr} = \frac{267.7}{(0.98)\ (800)} - (0.52)\ (0.122) = 0.28$$

$$E_{Sr} = \frac{272.3}{(.97)\ (800)} - (0.52)\ (0.122) = 0.29$$

Preparation of Gross Beta Standards

Principle

Gross beta determinations sacrifice accuracy for simplicity, and the selection of a reference radionuclide determines to a great extent the reliability of the obtained data. Self-absorption and counting efficiency depend upon a number of parameters, among them chemical composition of the compound and the radionuclides present.

The following materials were used to investigate of the use of proper reference radionuclides for the gross beta determination in food and soil ash:

(1) Food ash prepared from a mixture of several types of food representing a total diet of an average U.S. consumer.
(2) Soil from the eastern part of the United States. The soil was ashed to oxidize any organic compounds which may have been present.
(3) Vegetation ash.
(4) Milk ash.
(5) Wheat grain cereal ash.
(6) Residue of the evaporation of ocean water.

The selection of a reference radionuclide for gross beta determination is important. The aim of this investigation was to select a reference radionuclide which most nearly resembles the activity of the particular natural sample. The most accurate method would have been a radiochemical separation of all possible and conceivable radionuclides in the samples. However, this was too elaborate for the scope of this investigation. A simpler method with similar results is the comparison of the self-absorption of the sample with the self-absorption of the sample contaminated with the suspected radionuclide. The latter method has the advantage that it can be carried out in small laboratories with little radiochemical capability. Increasing amounts of the ashed sample are placed on a planchet and counted. The most likely radionuclide is then added to the ash and the procedure repeated.

It has been established that in times when no fresh fission products are in the atmosphere the major beta emitters detectable by gross activity determinations in the environmental samples are ^{90}Sr and ^{40}K.

Since carrier-free ^{40}K is not available, its substitution by natural potassium represents some uncertainties. The abundance of ^{40}K in natural potassium is only 0.10 percent. This necessitates the addition of a large amount of carrier potassium and an anion such as chloride. The results of the experiments described in this report indicate, however, that in some cases the use of potassium as the reference radionuclide is justified. Potassium is readily available and the small abundance of ^{40}K makes weighing errors less probable.

The similarity between the average energy of ^{40}K and ^{90}Sr-^{90}Y and their self-absorption curves up to a relatively long range permits the use of ^{90}Sr-^{90}Y for the calibration of counting instruments in low absorption regions (1 mg/cm^2) for ^{40}K with little error. Only higher carrier content would result in erroneous results.

At low carrier weights for different environmental samples, errors arising from the usage of any ash for weights not exceeding 1 mg/cm^2 are small. Silica gel has been used for these low weights as it is easy to handle and readily available. The best results were obtained using a compound with a mesh size above 325 (10 - 50 micron diameter). It contained no detectable activity and retained a constant weight over the required time. Silica gel may also be used as a substitute for ashed samples, when large quantities of ash are not available.

For the gross beta determination of food and vegetation, the procedure described for ^{40}K should be used as the reference method. For gross beta determinations of soil, ^{90}Sr (in equilibrium with its daughter product ^{90}Y) is the preferred radionculide. It should be noted that these conclusions do not necessarily apply to materials other than soil, food, vegetation and biota. Different contaminants in these materials, due to different sampling procedures and/or geographical origin, may require a different reference method.

Reagents

Potassium chloride
Silica gel (10-50 micron diameter mesh)
Strontium-90 standard
Ethanol (95 percent)

Procedure

Self-absorption curve of natural activity of ashed samples

1. Prepare duplicate samples on 5 cm planchet with the following approximate mg weights of ash or silica gel: 20, 40, 80, 120, 160, 200, 300, 400, 600, 1000, 3000, 5000.
2. Add 5-10 ml ethanol to each planchet.
3. Evaporate gently to dryness. (If an even distribution is not achieved the first time, add 5-10 ml of ethanol and evaporate gently to dryness).
4. Weigh the content of the planchet accurately (it should be kept in a desiccator).
5. Count.

Self-absorption curve of Potassium-40

Place 10 g of potassium chloride in a beaker and dissolve it in 50 ml of water. Add 50g of ash and stir thoroughly with a glass rod. Evaporate to dryness and follow the above procedure for natural activity (steps 1-5) by weighing aliquots of the dried material on planchets.

Self-absorption curve of Strontium-90 - Yttrium-90

Place 50 g of ash in a beaker, add 100 ml of ethanol and 1 ml of ^{90}Sr standard (2,000 dpm). Stir thoroughly with a glass rod and evaporate to dryness. Follow the preceding procedure for natural activity (steps 1-5).

Calculations

Since the natural activity of a sample is usually unknown, the self-absorption curve is prepared by calculating the cpm/mg of each planchet and plotting this against mg/cm^2. Extrapolate mg/cm^2 to zero and use this value as cpm/mg with no self-absorption. Counting losses at the various weights can be calculated and a subsequent curve can be drawn plotting percent loss versus mg/cm^2.

This curve is then used in the following equation relating measured counts to sample activity:

$$\text{pCi/g} = \frac{A}{(2.22)(B)(C)(D)},$$

where

A = net cpm,
B = counting efficiency in terms of cpm/dpm,
C = weight of sample in grams,
D = transmittance, as 1 - self-absorption, and
2.22 = dpm/pCi.

Preparation of Gross Alpha Standards

Most of the comments made for gross beta determination apply to the gross alpha activity determination. An additional complication is the short range of alpha particles and the varied energies of natural radioactivity.

For the preparation of the self-absorption curve, ^{239}Pu was selected as the reference radionuclide. Advantages of this radionuclide are (1) its energy of 5 MeV is an average between the naturally occurring alpha emitters, (2) the long half-life of the daughter product ^{235}U delays its production even in several years, and (3) plutonium has no beta and only small gamma emission.

The procedure for preparing standards for self-absorption curves is identical to that of ^{90}Sr-^{90}Y, replacing ^{90}Sr by ^{239}Pu.

Calculations

The gross alpha self-absorption curve is prepared exactly the same as that for gross beta. However, due to the short range of alpha particles, the infinite thickness is readily obtained and the specific activity is easily determined. It is not necessary to go beyond 2000 mg in weight.

Calculate the gross alpha activity from the following equation:

$$\text{gross alpha, pCi/g} = \frac{A}{(2.22)(B)(C)(D)},$$

where

A = net cpm,
B = counting efficiency in terms of cpm/dpm,
C = weight of sample in grams,
D = transmittance, 1 - self-absorption, and
2.22 = dpm/pCi.

For an infinitely thick sample, (2.22)(B)(C)(D) is a constant and this calculation is reduced to pCi/g = A K, where $K = \frac{1}{(2.22)(B)(C)(D)}$.

Notes

1. Metricel is a trademark of Gelman Sciences, Inc., Ann Arbor, Michigan.

References

1. Porter, C.R., Augustine, R.J., Matusek, J.M., Jr., and Carter, M.W., Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples, U.S. Department of Health, Education, and Welfare, Public Health Service Publication Number 999-RH-10 (1965).

RADIOCHEMICAL DETERMINATION OF AMERICIUM-241 IN ASHED SAMPLES

(Including Soil, Fly Ash, Ores, Vegetation and Biota)

Principle

The sample is ashed at 550°C for 72 hours. Americium-243 tracer is added to a weighed aliquot of sample. The sample is then solubilized with a mixture of HF and $HClO_4$. Plutonium and uranium are removed by extraction into triisooctylamine (TIOA). Thorium is removed by adsorption on anion exchange resin. Americium is extracted from nitric acid into dibutyl-N, N-diethyl carbamyl phosphonate (DDCP). The americium is stripped from DDCP with dilute nitric acid and coprecipitated with 0.1 mg lanthanum as fluoride. The actinide is radioassayed by alpha spectroscopy.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Suction filter for 25 mm membrane.
3. Plastic graduated cylinder, 100 ml volume.
4. Separatory funnels, 1 liter capacity.
5. Planchets, stainless steel, 32 mm diameter.
6. Alpha spectrometric system consisting of multichannel analyzer biasing electronics, printer, silicon surface barrier detectors, vacuum pump and chamber.
7. Teflon beakers. See Note 2.
8. Ion exchange column, 2 cm diameter, 10.5 cm length.

Reagents

1. Americium-243 tracer solution. Approximately 1 pCi per ml, calibrated.
2. Anion exchange resin. BioRad AG1X8 or equivalent (200-400 mesh, nitrate form). Convert to nitrate form for thorium separation by

washing the resin with 6M HNO_3 until the washing shows no trace of chloride when tested with $AgNO_3$. See Note 3.

3. Dibutyl-N, N-diethyl carbamyl phosphonate (DDCP). See Note 4.
4. Hydrochloric acid, 12M, 37 percent HCl reagent.
5. Hydrochloric acid, 9M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
7. Hydrofluoric acid, 29M, 48 percent HF reagent.
8. Hydrofluoric acid, 3M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduate and storage bottle.
9. Hydrogen peroxide, 50 percent reagent grade.
10. Lanthanum carrier, 0.1mg La^{+3} per ml. Dissolve 0.0799g
11. $La(NO_3)_3 \bullet 6H_2O$ per 250 ml 1M HCl.
12. Nitric acid, 16M, 70 percent HNO_3 reagent.
13. Nitric acid, 12M. Dilute 750 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
14. Nitric acid, 6M. Dilute 375 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
15. Nitric acid, 2M. Dilute 167 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
16. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
17. Silver nitrate, crystalline reagent.
18. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Add 1 ml 6M HNO_3 and dilute to 100 ml with distilled water.
19. Triisooctylamine (TIOA), reagent grade.
20. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
21. p-Xylene, reagent grade.

Sample Preparation

1. Add weighed 1 gram aliquot of ashed sample to Teflon beaker.
2. Add measured aliquot of americium-243 tracer solution.
3. Add 15 ml of 29M HF and evaporate to dryness. Repeat this step two more times to volatilize silica as SiF_4.
4. Add 5 ml of 12M $HClO_4$ and 5 ml of 9M HCl. Evaporate to dryness and repeat this step.
5. Add 10 ml 12M HCl and dissolve residue.
6. Transfer sample to 400 ml glass beaker, washing Teflon beaker with 9M HCl.
7. Evaporate solution in glass beaker to dryness. Add 10 ml 12M HCl and repeat this step. Avoid baking solids.

Determination

1. Dissolve sample by adding 100 ml 9M HCl and warming beaker to maximum of 50°C.
2. Add 2 ml 50 percent H_2O_2. Heat gently and set aside for 10 minutes.
3. Place 100 ml 10 percent TIOA in 500 ml separatory funnel. Add 50 ml 9M HCl and shake for one minute to equilibrate. Allow phases to separate cleanly and draw off and discard lower aqueous acid phase.
4. Add sample to TIOA in separatory funnel and shake for two minutes. Vent funnel stopcock frequently to avoid pressure build-up in funnel.
5. Allow phases to separate cleanly. Draw off and save aqueous acid phase.
6. Add 50 ml 9M HCl to TIOA solution to separatory funnel and shake for 1 minute.
7. Allow phases to separate and drain 9M HCl wash into beaker containing acid from step 5.
8. Repeat steps 6 and 7.

9. Put combined acid phases in clean 500 ml separatory funnel and add 100 ml p-xylene to funnel. Shake for one minute.
10. Allow phases to separate cleanly and drain off aqueous acid phase into clean beaker.
11. Add 10 ml 16M HNO_3 and 5 ml 12M $HClO_4$ to aqueous acid phase and evaporate to near dryness. Do not overheat solids.
12. Add 10 ml 16M HNO_3 and evaporate to near dryness.
13. Dissolve sample in 50 ml of 6M HNO_3 with warming.
14. Prepare ion exchange column with 25 ml of anion exchange resin. Wash resin with 100 ml of 6M HNO_3.
15. Place sample in 125 ml separatory funnel on top of column acting as reservoir.
16. Allow sample to flow through column at the rate of approximately 2 ml per minute. Collect eluate and do not allow column to run dry.
17. Flow 100 ml 6M HNO_3 through column after sample has passed through. Collect in same beaker as sample.
18. Evaporate eluate just to dryness and allow beaker containing residue to cool.
19. Add 20 ml distilled water to residue and swirl to dissolve residue. The solution may not appear completely clear at this step.
20. Add 10 ml of 16M HNO_3 to the solution and heat to near boiling.
21. Remove the solution from the hot plate and add 10 ml of 16M HNO_3.
22. Pour the solution into a 125 ml separatory funnel and rinse the beaker with two 10 ml volumes of 16M HNO_3. Transfer rinses to funnel.
23. Allow the solution to cool to ambient temperature and add 1 ml of DDCP.
24. Shake the separatory funnel vigorously for 15 seconds.

25. Allow the layers to separate for at least 2 hours or overnight if possible.
26. Drain and discard the aqueous (lower) layer.
27. Add 10 ml of 12M HNO_3 into the funnel and shake for 5 seconds.
28. Allow 1 hour for the layers to separate, drain and discard the lower rinse solution. See Note 5.
29. Add 10 ml p-xylene to the DDCP in the separatory funnel.
30. Add 20 ml of 2M HNO_3 to the funnel and shake vigorously for 15 seconds.
31. Allow the layers to separate for at least 30 minutes and drain strip solution into a 100 ml beaker.
32. Repeat step 30 and combine second strip solution with first.
33. Place combined 2M HNO_3 strip solution in clean 125 ml separatory funnel.
34. Add 25 ml p-xylene to funnel and shake for 15 seconds.
35. Allow phases to separate and drain lower layer into clean 100 ml beaker.
36. Evaporate strip solution just to dryness.
37. Add 10 ml 16M HNO_3 and 5 ml 12M $HClO_4$ to beaker and evaporate to dryness.
38. Add 10 ml 12M HCl and evaporate to near dryness.
39. Take up residue in 50 ml 1M HCl.
40. Heat on water bath to 80°C with stirring.
41. Suspend clean nickel foil strip into solution for two hours to remove traces of polonium.
42. Remove nickel strip and evaporate solution to dryness.
43. Add 15 ml 1M HCl to beaker and warm to dissolve residue.
44. Coprecipitate americium fluoride by adding 1 ml of lanthanum carrier and 5 ml 3M HF. Mix well and set aside for 30 minutes.
45. Filter coprecipitated sample through a filter membrane with suction.
46. Rinse sample beaker with water and add to filter funnel.

47. Rinse beaker with alcohol and add to funnel. Wash funnel with alcohol.
48. Disassemble filter funnel when membrane is dry. Mount membrane on a 32 mm planchet using double stick tape.
49. Radioassay sample for americium-241 in alpha spectrometer.

Calculations

Calculate the concentration, Z, of americium-241 in picocuries per gram as follows:

$$Z = \frac{(A-A_1)(F)}{(2.22)(B-B_1)(E)(W)(T)}$$

where

A = gross sample counts which appear in the americium-241 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
F = total calibrated tracer counts for same counting time as sample counts,
2.22 = dpm per pCi,
B = gross tracer counts which appear in the alpha energy region of the tracer isotope,
B_1 = background counts in the same alpha energy region as B above,
E = alpha detector efficiency,
W = sample weight (grams), and
T = counting time (minutes).

Calculate the lower limit of detection (LLD) in picocuries per gram as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(W)(T)}$$

where

C_B = background count rate,
T = counting time,
2.22 = dpm per pCi,
E = alpha detector efficiency,
R = fractional yield based on $B-B_1/F$ in calculation, and
W = sample weight (grams).

This LLD calculation is valid if the sample counting time is equal to the background counting time.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.
2. Teflon is a registered trademark of DuPont Co., Wilmington, DE.
3. Thorium in the sample may be determined by washing the resin with water and measuring the thorium in the wash.
4. DDCP is currently available from Columbia Organic Chemical Company, Columbia, SC.
5. When draining the separatory funnel always allow a small quantity of aqueous phase to remain in funnel. Avoid letting organic phase into stopcock.
6. If plutonium analysis is attempted sequentially with americium, the plutonium-242 tracer should be checked for plutonium-241 content. This isotope decays to americium-241.

References

1. Moore, F. L., "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric Acid Solution with Tri (iso-octyl) amine," Analytical Chemistry 30, 908 (1958).
2. Butler, F. E., "Determination of Actinides in Biological Samples with Bidenate Organophosphorus Extractant," Analytical Chemistry 42, 1073 (1970).

RADIOCHEMICAL DETERMINATION OF CARBON-14 IN AQUEOUS SAMPLES

Principle

Carbon carrier in the form of sodium oxalate is added to an unacidified aqueous sample in a closed distillation apparatus. An oxidizing agent and acid are added to the sample to convert carbon compounds to CO_2. Nitrogen is slowly bubbled through the sample and heat is applied to transfer the CO_2 into a flask containing a basic $CaCl_2$ solution. The collected $CaCO_3$ is centrifuged, washed, transferred to a planchet, weighed, and counted.

Special Apparatus

1. Low background beta particle counter with a window less than 2 mg/cm^2 thickness.
2. Centrifuge.
3. Stainless steel planchets, 5 cm diameter.
4. Infrared heat lamp.
5. Distillation apparatus (see Figure 1).

Reagents

1. Ammonium hydroxide, 15 M. NH_4OH reagent.
2. Ammonium hydroxide, 0.1 M. Dilute 6.7 ml of the NH_4OH reagent to 1 liter with distilled water.
3. Calcium chloride, crystalline reagent.
4. Calcium chloride, 1.5 M. Dissolve 166.5 g $CaCl_2$ reagent in 700 ml distilled water and dilute to 1 liter with distilled water.
5. Potassium permanganate, crystalline reagent.
6. Potassium permanganate, 0.5 M. Dissolve 79.0 g $KMnO_4$ reagent in 700 ml distilled water and dilute to 1 liter with distilled water.
7. Sodium oxalate, crystalline reagent.
8. Sodium oxalate carrier, 0.1 M. Dissolve 13.4 g $Na_2C_2O_4$

reagent in distilled water and dilute to 1 liter with distilled water. See Note 1.

9. Sulfuric acid, 18 M. 96 percent H_2SO_4 reagent.
10. Sulfuric acid, 9 M. Dilute 500 ml H_2SO_4 to 1 liter with distilled water.

Procedure

1. Add 1 ml $Na_2C_2O_4$ solution to a 200 ml neutral or basic sample in a distillation flask.
2. Start a slow bubbling of nitrogen or CO_2-free air through the solution and connect the distilling outlet to a 200 ml receiving flask containing 100 ml 0.1 M NH_4OH and 1 ml 1.5 M $CaCl_2$.
3. With the system closed, add 1 ml 0.5 M $KMnO_4$ and 5 ml 9 M H_2SO_4 through the separatory funnel to the distilling flask and swirl to mix contents.
4. Heat flask and boil contents gently for 30 minutes while bubbling the N_2 (or air) through the distilling and receiving flasks.
5. Transfer the precipitated $CaCO_3$ from the receiving flask to a centrifuge tube. Centrifuge and discard supernatant solution.
6. Wash precipitate twice with 15 ml aliquots of boiled distilled water and discard wash solutions.
7. Take up precipitate in 5 ml boiled distilled water and transfer quantitatively to a weighed stainless steel planchet.
8. Dry precipitate under a heat lamp, cool, and weigh. Compute chemical yield based on the total weight of $CaCO_3$ formed.
9. Count with a thin window beta particle counter (< 2 mg/cm^2).

Calculation

Calculate the concentration, Z, of carbon-14 in picocuries per milliliter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(E)(V)(R)}$$

where

C_1 = gross count/minute of sample,
C_B = background counts/minute,
E = beta particle counter efficiency,
V = sample volume (ml),
R = fractional chemical yield, and
2.22 = dpm/pCi.

Calculate the lower limit of detection (LLD) for carbon-14 in picocuries per milliliter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(V)(R)(T)}$$

where

C_B = background counts/minute,
E = beta particle counter efficiency,
V = sample volume (ml),
R = fractional chemical yield,
T = counting time, and
2.22 = dpm/pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. The $Na_2C_2O_4$ should be standardized frequently by distillation with boiled distilled water. One ml of 0.1 M $Na_2C_2O_4$ is equivalent to 20 mg $CaCO_3$. The standardized value will include any CO_2 absorbed by the carrier solution upon standing.

References

1. Krieger, H.L., and Gold, S., Procedure for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions, EPA-R4-73-014, May 1973.

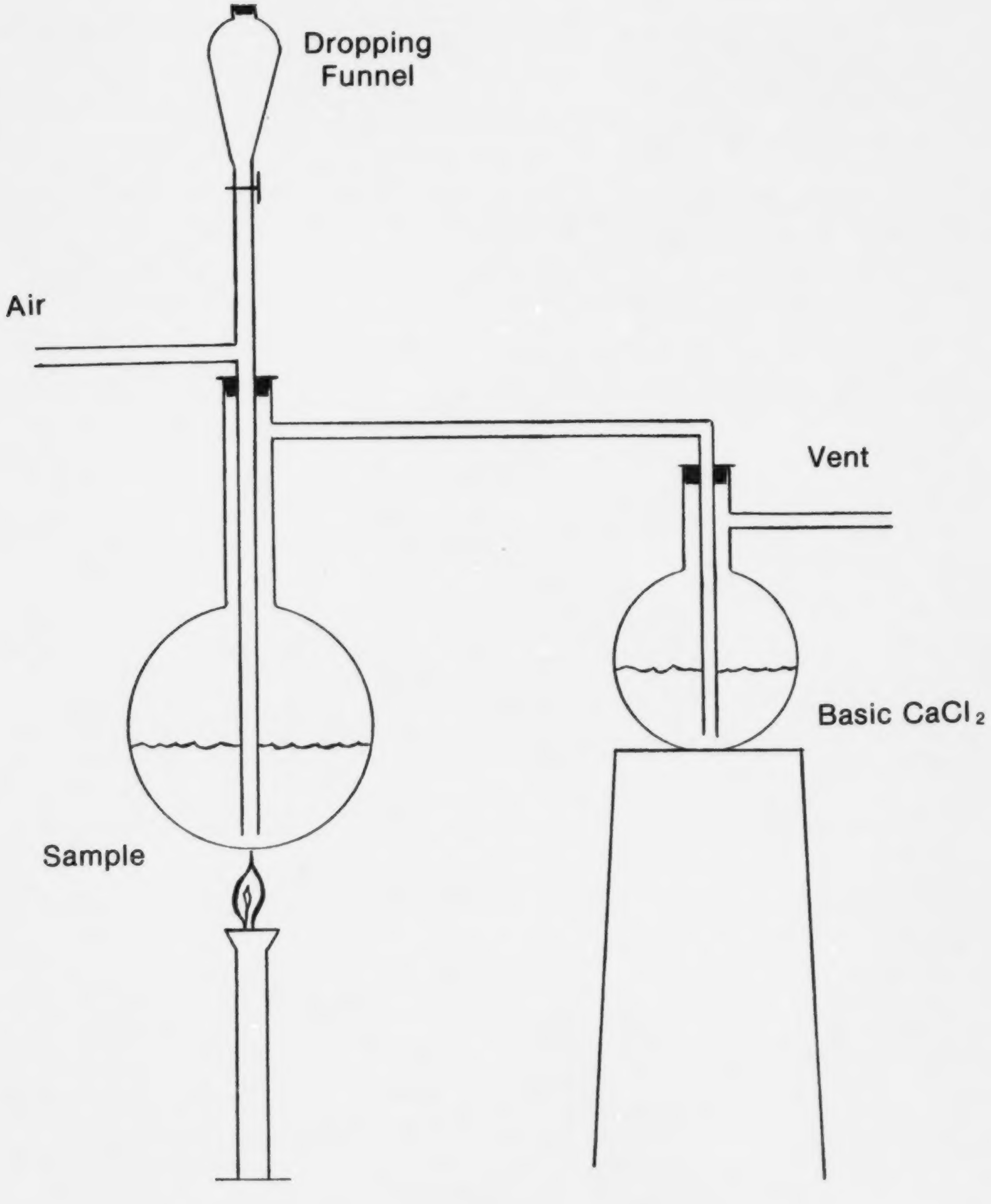
Dropping Funnel
Air
Vent
Basic $CaCl_2$
Sample

Figure 1. Carbon-14 distillation apparatus.

RADIOCHEMICAL DETERMINATION OF TRITIUM IN MILK, SOIL, URINE, VEGETATION AND OTHER BIOLOGICAL SAMPLES

Azeotropic Method

Principle

Tritium activity in the water content of a sample is radioassayed after separating the water from the sample by a cyclohexane-water azeotropic distillation. A measured aliquot of the sample is heated in an azeotrope still together with cyclohexane. The separated water is measured and counted for tritium using a liquid scintillation spectrometer.

Special Apparatus

1. Azeotropic still. See Figure 1.
2. Liquid scintillation counter, ambient temperature operation. See Note 1.
3. Low background counting vials, 25 ml capacity. See Note 2.

Reagents

1. p-Bis (o-methylstyryl) benzene (bis MSB).
2. Cyclohexane, spectrophotometric grade reagent.
3. Desiccant, calcium chloride type.
4. 2,5-Diphenyloxazole (PPO).
5. Scintillation solution. Dissolve 7.0 g of 2,5-diphenyloxazole (PPO) and 1.5 g of p-bis (o-methylstyryl) benzene (bis MSB) in 1 liter of p-xylene. Mix this solution with Triton N101 in a volume ratio of 2.75 parts of p-xylene solution to 1 part of Triton N101. The correct volume of Triton N101 is 364 ml for each liter of p-xylene. Store the solution in a brown bottle and protect from sunlight.
6. Tritiated water standard containing nominally 5 X 10^5 dpm ^3H/ml known to 3 percent accuracy.

7. Triton N101, Rohm and Haas Co., Philadelphia, PA. See Note 3.
8. p-Xylene, scintillation grade reagent.

Procedure

1. Add measured sample and cyclohexane to distillation flask using amounts shown in Table 1.
2. Assemble distillation apparatus and heat sample flask until water stops collecting in receiver.
3. Stop distillation and measure volume of collected water.
4. Place 10 ml aliquot of collected water in liquid scintillation vial and add 15 ml scintillation solution.
5. Prepare blank solution with low tritium water using same volume of water as sample.
6. Prepare standard solution of tritiated water with same volume of water as sample.
7. Place sample vials in liquid scintillation counter and allow vials to dark adapt for one hour before starting counting sequence.

Calculations

Calculate the concentration, Z, of tritium in picocuries per sample as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(E)(V)}$$

where

C_1 = gross beta counts per minute,
C_B = scintillation counter background counts per minute,
E = counting efficiency,
V = sample size, and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries per sample as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(T)(V)}$$

where

C^B = background count rate,
T = counting time,
E = counting efficiency,
V = sample size, and.
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. For optimum performance of the scintillation solution, the temperature of the counting instrument should be kept should be between 18 and 25°C.
2. Low potassium glass or plastic vials should be used to minimize background counts. Plastic vials should be resistant to the scintillation solution. The solvent, p-xylene, will migrate through the plastic vials, therefore the samples should be counted no longer than three days after preparation.
3. Triton N101 is a tradename for a nonylphenol polyethylene glycol ether.

References

1. W. M. Jones, J. Chemical Physics, 48, 207 (1968).

2. 1969 Book of ASTM Standards, Part 18, 2nd ed., American Society for Testing and Materials, pp. 16-19.
3. R. Lieberman and A. A. Moghissi, Inter. J. Appl. Rad. Isotopes, 21, 319 (1970).
4. A. A. Moghissi, E. W. Bretthauer, and E. H. Compton, Analytical Chemistry, 45 1965, (1973).
5. A. A. Moghissi, Health Physics, 41, 413, (1981).

TABLE 1

Sample Sizes and the Quantity of Cyclohexane Required for Various Sample Types

Sample Type	Sample Size	Cyclohexane (ml)
Soil	200 g	1300
Hay	50 g	400
Green Chop	30 g	70
Biological Tissue	30 g	150
Urine	20 ml	50
Milk	30 ml	70

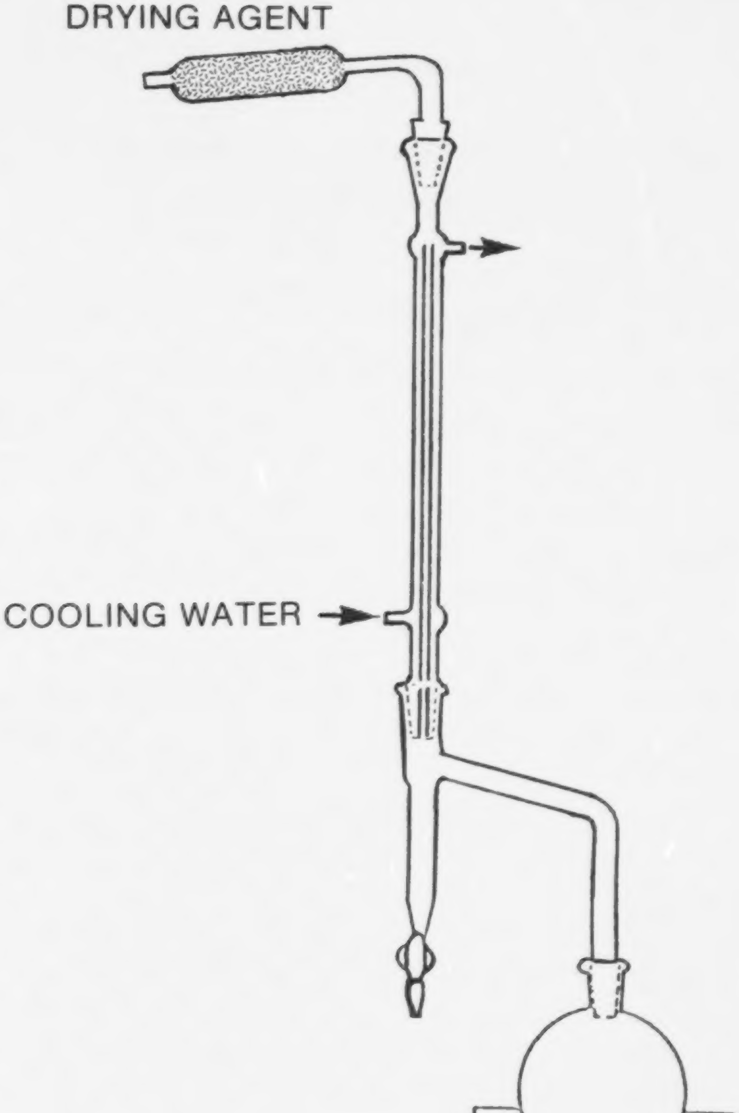
DRYING AGENT
COOLING WATER
HEATER

Figure 1. Azeotrope still.

RADIOCHEMICAL DETERMINATION OF TRITIUM IN WATER

Dioxane Method

Principle

Water samples that have been distilled are incorporated into a counting mixture consisting of dioxane, naphthalene, and fluors. The tritium is assayed on a liquid scintillation spectrometer.

Special Apparatus

1. Liquid scintillation counter.
2. Low background counting vials.
3. Sample distillation glassware.

Reagents

1. p-Bis (o-methylstyryl) benzene (bis MSB).
2. p-Dioxane, scintillation grade.
3. 2,5-Diphenyloxazole (PPO).
4. Desiccant, calcium sulfate type.
5. Naphthalene, scintillation grade.
6. Tritiated water standard containing nominally 5×10^5 dpm ^3H/ml known to 3 percent accuracy.
7. Scintillation solution. Dissolve 7.0 g of 2,5 diphenyloxazole (PPO), 1.5 g p-bis (o-methylstyryl) benzene (bis MSB) and 120 g naphthalene in 800 ml p-dioxane and dilute to 1 liter with p-dioxane. Store the solution in a brown bottle and protect from sunlight.

Procedure

1. Distill aqueous sample in glass. Collect enough distillate for at least two determinations.
2. Dispense 16 ml of the above scintillation solution into a

counting vial. Add 4 ml of the distilled aqueous sample, cap vial and shake to mix contents.

3. Prepare standards and backgrounds identical to the samples using low tritium water, if available, for preparing background samples.
4. Place sample vials in liquid scintillation counter and allow vials to dark adapt for one hour before starting counting sequence.
5. Count samples in duplicate for at least 50 minutes each.

Calculations

Calculate the concentration, Z, of tritium in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(E)(V)}$$

where

C_1 = gross beta counts per minute,
C_B = scintillation counter background counts per minute,
E = counting efficiency,
V = volume of water (liters), and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(T)(V)}$$

where

C_B = background count rate,

T = counting time,
E = counting efficiency,
V = sample size (liters), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

References

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RADIOCHEMICAL DETERMINATION OF TRITIUM IN WATER

Emulsion Method

Principle

Water samples that have been distilled are incorporated into a counting mixture consisting of a primary solvent, emulsifier, and fluors. The tritium is assayed on a liquid scintillation spectrometer.

Special Apparatus

1. Liquid scintillation counter, ambient temperature operation. See Note 1.
2. Low background counting vials, 25 ml capacity. See Note 2.
3. Sample distillation glassware.

Reagents

1. p-Bis (o-methylstyryl) benzene (bis MSB).
2. 2, 5 - Diphenyloxazole (PPO).
3. Desiccant, calcium sulfate type.
4. Tritiated water standard containing nominally 5 x 10^5 dpm ^3H/ml known to 3 percent accuracy.
5. Triton N101, Rohm and Haas Co., Philadelphia, PA. See Note 3.
6. p-Xylene, scintillation grade reagent.
7. Scintillation solution. Dissolve 7.0 grams of 2, 5 - diphenyloxazole (PPO) and 1.5 grams of p-bis (o-methylstyryl) benzene (bis MSB) in one liter of p-xylene.
   Mix the above solution and Triton N101 in a volume ratio of 2.75 parts of p-xylene to 1 part of Triton N101. The correct volume of Triton N101 is 364 ml for each liter of p-xylene. Store the solution in a brown bottle and protect from sunlight.

Procedure

1. Distill aqueous sample in glass. Collect enough (>25 ml) distillate for at least two determinations.
2. Dispense 15 ml of the above scintillation solution into a 25 ml counting vial. Add 10 ml of the distilled aqueous sample, cap vial and shake to mix contents. See Note 4.
3. Prepare standards and backgrounds identical to the samples using low tritium water, if available, for preparing background samples.
4. Place sample vials in liquid scintillation counter and allow vials to dark adapt for one hour before starting counting sequence.
5. Count each sample in duplicate for at least 50 minutes each.

Calculations

Calculate the concentration, Z, of tritium in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(E)(V)}$$

where

C_1 = gross beta counts per minute,
C_B = scintillation counter background counts per minute,
E = counting efficiency,
V = volume of water (liters), and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(T)(V)}$$

where

C_B = background count rate,
T = counting time,
E = sample size (liters), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. For optimum performance of the scintillation solution, the temperature of the counting instrument should be kept should be between 18 and 25°C.
2. Low potassium glass or plastic vials should be used to minimize background counts. Plastic vials should be resistant to the scintillation solution. The solvent, p-xylene, will migrate through the plastic vials, therefore the samples should be counted no longer than three days after preparation.
3. Triton N101 is a brand name for a nonyl phenol polyethylene glycol ether.
4. Smaller vials can be used, keeping the added aqueous sample at 40 percent of the capacity of the vial, and scintillation solution at 60 percent.

References

1. Lieberman, R. and Moghissi, A. A., "Low-level counting by Liquid Scintillation, II. Application of Emulsions in Tritium Counting," Inter. J. Appl. Rad. Isotopes, 21, 319 (1970).

RADIOCHEMICAL DETERMINATION OF IODINE-131 IN DRINKING WATER

Principle

Stable iodate carrier is added to an acidified sample of drinking water. After reduction to the iodide state by Na_2SO_3, the radioiodine is precipitated as AgI. The precipitate is dissolved and purified by addition of zinc powder and sulfuric acid. The iodine is reprecipitated as PdI_2 for radioassay.

Special Apparatus

1. Low background beta counter.
2. Centrifuge.
3. Electric hot plate.
4. Suction filter apparatus for 25 mm filter membranes.
5. Metricel DM800 membrane filters, 25mm diameter, 0.8 micrometer pore size or equivalent. See Note 1.
6. Stainless steel planchets, 5 cm diameter.
7. Glassware
8. Analytical balance.

Reagents

1. Ammonium hydroxide, 15M. Reagent grade NH_4OH.
2. Ammonium hydroxide, 6M. Mix 400 ml 15M NH_4OH with 600 ml distilled water.
3. Ethanol, 95 percent reagent.
4. Hydrochloric acid, 12M, 37 percent HCl reagent.
5. Hydrochloric acid, 6M. Dilute 500 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Iodate carrier, 10 mg IO_3^-/ml. Dissolve 12.24 g KIO_3 in 900 ml distilled water and dilute to 1 liter with distilled water. See Note 2 for standardization.
7. Nitric acid, 16M, 70 percent HNO_3 reagent.

8. Nitric acid, 0.4M. Dilute 25 ml reagent grade HNO_3 to 1 liter with distilled water.
9. Palladium chloride, 0.2M. Dissolve 3.55g $PdCl_2 \cdot 2H_2O$ in 90 ml distilled water and dilute to 100 ml with distilled water.
10. Silver nitrate, 0.1M. Dissolve 16.99g $AgNO_3$ in 900 ml distilled water and dilute to 1 liter with distilled water.
11. Sodium sulfite, 1M. Dissolve 12.6g Na_2SO_3 in 90 ml distilled water and dilute to 100 ml with distilled water. Prepare fresh daily.
12. Sulfuric acid, 1M. Dilute 56 ml of the 96 percent reagent grade H_2SO_4 to 1 liter with distilled water.
13. Zinc, reagent grade powder.

Procedures

1. To a 2 liter drinking water sample add 15 ml 16M HNO_3 and 1 ml iodate carrier and mix well.
2. Add 4 ml freshly prepared 1M Na_2SO_3 and stir for 30 minutes.
3. Add 20 ml 0.1 M $AgNO_3$, stir for one hour and allow precipitate formed to settle for another hour.
4. Decant as much supernate as possible without losing any precipitate and discard.
5. Filter the remaining liquid through a filter membrane and discard filtrate.
6. Transfer the filter membrane and precipitate (AgI) to a centrifuge tube and slurry with 10 ml water.
7. Add 1 gram zinc powder and 2 ml 1M H_2SO_4 and stir frequently for 30 minutes.
8. Filter mixture from step 7 with suction using a filter membrane and collect filtrate in a centrifuge tube. Use five ml water to wash residue and filter chimney. Discard residue.
9. Add 2 ml 6M HCl to filtrate and heat tube containing filtrate in a water bath at 60°C.

10. Add 1 ml 0.2 M $PdCl_2$ and digest for at least five minutes while heating.
11. Centrifuge and discard supernate.
12. Dissolve the precipitate in 5 ml 6M NH_4OH and heat in a boiling water bath until clear.
13. Filter solution from step 12 with suction using a filter membrane or equivalent. Collect filtrate in a centrifuge tube washing the residue and filter chimney with 5 ml water. Discard residue.
14. Add 6M HCl to filtrate from step 13 until color changes to yellow, using approximately 2 ml 6M HCl. Add an additional 2 ml 6M HCl and heat to 60°C in a water both.
15. Add 1 ml 0.2M $PdCl_2$ to reprecipitate PdI_2 and digest on the water bath for ten minutes. Cool slightly.
16. Filter through a tared filter membrane transferring precipitate from tube to filter with water. Wash precipitate with 5 ml aliquots of water and ethanol.
17. Dry precipitate at 70°C for 30 minutes to constant weight and weigh to the nearest 0.1 mg.
18. Place filter on planchet and count on a low background beta counter for 1000 minutes.

Calculations

Calculate the concentration, Z, of iodine-131 in picocuries per liter as follows:

$$Z = \frac{C}{(2.22)(A)(E)(V)(R)}$$

where

C = net count rate, counts per minute,
A = decay correction for iodine-131 (half-life = 8.04 days),
E = counter efficiency,

V = sample volume (liters),
R = fractional chemical yield based on weight of PdI_2, and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries of iodine-131 per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(T)(V)}$$

where

C_B = background count rate,
E = beta counter efficiency,
R = fractional chemical yield based on weight of PdI_2,
T = counting time (same for sample and background),
V = sample size (liters), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is approximately equal to the background counting time.

Notes

1. Metricel is a trademark of Gelman Sciences Inc., Ann Arbor, MI.
2. Standardization of Iodate Carrier. Pipette 1.0 ml potassium iodate (KIO_3) carrier into a 50 ml centrifuge tube containing 10 ml 0.4$\underline{M}$ HNO_3. Add 1 ml 1$\underline{M}$ Na_2SO_3 and stir in a water both for 5 minutes. Add 1 ml 0.2 $\underline{M}$ $PdCl_2$ to precipitate and coagulate PdI_2. Cool and filter through a tared filter membrane. Dry to constant weight at 70°C, cool and weigh as PdI_2.

References

1. Krieger, Herman L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, (1980).
2. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.

RADIOCHEMICAL DETERMINATION OF IODINE-131 IN MILK

Principle

The milk is preserved at sampling by adding formalin containing iodide carrier. The milk sample is stirred with anion exchange resin and the iodine is eluted from the resin after oxidation to IO_3^- with hypochlorite solution. After reduction, the iodine is extracted into CCl_4, reduced with bisulfite, and back-extracted into water. The iodine is then precipitated as PdI_2. Chemical yield based on added iodine carrier is determined gravimetrically. The iodine-131 is measured by counting in a low background beta counter.

Special Apparatus

1. Metricel DM 800 filter membranes or equivalent, 25 mm diameter, 0.8 micrometer pore size. See Note 1.
2. Magnetic stirrer and stirring bars, 6 cm.
3. Stainless steel planchets, 5 cm diameter.
4. Suction filtering apparatus for 25 mm filter membranes.
5. Low background beta counter.
6. Separatory funnel, 500 ml capacity.
7. Glassware.

Reagents

1. Anion exchange resin. Dowex 1X8, 50-100 mesh, or equivalent, Cl^-/form. See Note 2.
2. Carbon tetrachloride, reagent grade.
3. Formalin, 37 percent formaldehyde solution, reagent grade.
4. Hydrochloric acid, 12M, 37 percent HCl reagent.
5. Hydroxylamine hydrochloride, reagent grade crystals.
6. Iodide carrier, 10 mg I^-/ml. Dissolve 1.8 g reagent grade NaI in 100 ml distilled water.
7. Palladium chloride, 10 mg Pd^{+2}/ml. Dissolve 2.0 g $PdCl_2\ 2H_2O$ in 100 ml distilled water.

8. Sodium bisulfite, 1M. Dissolve 1.04 g of $NaHSO_3$ in 10 ml distilled water. Prepare fresh daily.
9. Sodium chloride, 2M. Dissolve 116.9 g NaCl in 900 ml distilled water and dilute to 1 liter with distilled water.
10. Sodium hypochlorite, 5 percent (commercial laundry bleach).

Preservation of Milk Sample

Add 80 ml formalin containing 2 ml of iodide carrier to four liters of milk. Add 5 drops of freshly prepared 1M $NaHSO_3$ to each four liter sample.

Procedure

1. Pour a 4 liter milk sample into a 4 liter beaker and add a 50 ml volume of anion exchange resin stirred with 20 ml water.
2. Place a 6 cm magnetic stirring bar into the beaker and stir vigorously for 20 minutes.
3. Remove the stirring bar and allow the resin to settle to the bottom of the beaker, waiting 20 minutes.
4. Carefully decant the milk into a second 4 liter beaker leaving the ion exchange resin behind. Wash the resin with distilled water into a 600 ml beaker and save.
5. Place the magnetic stirring bar into the second 4 liter beaker, add a second 50 ml water slurry of anion exchange resin to the milk and stir vigorously for 20 minutes.
6. Remove the stirring bar and wait 20 minutes for the resin to settle.
7. Carefully decant and discard the milk.
8. Wash the second batch of resin into the 600 ml beaker containing the resin from step 4. When the combined resin has settled, decant and discard the supernatant water.
9. Add 300 ml hot water, 80-90°C, to the combined resin, stir briefly, and allow the resin to settle completely. Decant

aqueous portion. Repeat the hot water wash two more times.

10. Add 100 ml 5 percent NaOCl to the resin. Place a 2 cm magnetic stirring bar in the beaker and stir vigorously for five minutes on a magnetic stirrer.
11. Filter the resin slurry through a filter membrane into a 1 liter beaker and retain the NaOCl solution. See Note 3.
12. Transfer resin with 100 ml 5 percent NaOCl to a 200 ml beaker. Stir and filter as described in steps 10 and 11. Discard the resin.
13. Combine the two 100 ml solutions of NaOCl in the 1 liter beaker and carefully add 40 ml 16M HNO_3. See Note 4.
14. Pour the acidified NaOCl solution into a 500 ml separatory funnel and add 100 ml CCl_4.
15. Add 2 g of $NH_2OH \bullet HCl$ and shake. See Note 5.
16. Extract the iodine into the CCl_4 by shaking the separatory funnel for two minutes. See Note 6.
17. Drain the lower organic phase into a clean 500 ml separatory funnel and save.
18. Add 100 ml CCl_4 and 1 g $NH_2OH \bullet HCl$ to the aqueous phase in the separatory funnel and shake the funnel for two minutes.
19. Combine the organic phases and discard the aqueous phase.
20. Add 50 ml water and 0.5 ml of freshly prepared 1M $NaHSO_3$ to the separatory funnel containing the combined CCl_4 to reduce I_2 to I^- and shake for two minutes. Discard the lower organic phase. See Note 7.
21. Transfer the aqueous phase into a clean 100 ml beaker and add 1 ml 12M HCl and 10 ml of $PdCl_2$ solution. Stir to precipitate PdI_2 and set aside for five minutes.
22. Filter with suction through a tared filter membrane using a water wash to effect the transfer.
23. Dry the filter membrane and precipitate for 20 minutes at 110°C and weigh to the nearest 0.1 mg.

24. Mount the filter on a planchet and count in a low background beta counter for 1000 minutes.
25. If net count rate is greater than 0.3 counts per minute, recount the sample after eight days to confirm the presence of iodine-131 by decay.
26. Calculate the iodine-131 as piocuries per liter of milk at the time of sampling. See Note 8.

Calculations

Calculate the concentration, Z, of iodine-131 in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(A)(E)(V)(R)}$$

where

C_1 = gross beta counts per minute,
C_B = counter background counts per minute,
A = decay correction for iodine-131 (half-life = 8.04 days),
E = beta counter efficiency,
V = volume of milk (liters),
R = fractional chemical yield based on weight of PdI_2 recovered, and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries per liter as follows:

$$\text{LLD} = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(T)(V)}$$

where

C_B = background count rate,

T = counting time (same for sample and background),
E = beta counter efficiency,
R = fractional chemical yield based on weight of PdI_2,
V = sample size (liters), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. Metricel is a trademark of Gelman Sciences, Ann Arbor, MI.
2. Resin should be treated to remove any fines. This is accomplished by washing with water and allowing the resin to settle for five minutes before decanting the water. Repeat until the fines are removed.
3. Resin should have a very light straw color after the NaOCl extraction. If not, the NaOCl is not fresh and should be replaced.
4. Add the acid slowly with stirring until the vigorous reaction subsides. Use a hood for this step, to remove chlorine gas.
5. Proceed with caution in step 15. Excessive gas formation during the extraction can cause the stopcock or stopper of the separatory funnel to disengage with loss of sample. Start by gently swirling the solution to effect mixing. Invert the separatory funnel with funnel stem pointing up. Relieve the pressure by opening the stopcock and repeat this pressure-release step several times during shaking.
6. Organic phase should be deep red. If not, shake sample again after a few minutes. Repeat this waiting period, if necessary.
7. After back extraction into the water, the CCl_4 should be colorless. If not, add additional 1M $NaHSO_3$ and re-extract.
8. Milk samples may contain as much as 3 mg I^- which would add to the yield. It may be necessary to determine I^- in milk with a specific ion electrode. Iodide-specific electrodes are available from laboratory supply companies.

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RADIOCHEMICAL DETERMINATION OF KRYPTON-85 IN ENVIRONMENTAL AIR SAMPLES

Principle

Krypton is separated from other air constituents by passing approximately one cubic meter of air spiked with ^{83m}Kr through a charcoal trap at liquid nitrogen temperature and reduced pressure. The greater part of the nitrogen and oxygen pass through the trap while krypton and some of the other noble gases are concentrated. The remaining nitrogen is removed by reaction with titanium at elevated temperature. The noble gases are then transferred to a molecular sieve trap and cryogenically fractionated. The krypton is collected on a small amount of charcoal and subsequently transferred to a glass liquid scintillation vial for counting.

Special Apparatus

1. Air spiking system (Figure 1).
2. Krypton separation system (Figure 2).
3. Glass liquid scintillation vials with Teflon valves and Luer taper fittings (Figure 3).
4. Liquid scintillation counter.
5. Large volume heavy duty balloons to hold one cubic meter of air. The air spiking system and the krypton separation system are constructed with copper tubing and brass ferrule-type fittings.

The only glass in the systems are the flow meters, Dewar flasks, and the liquid scintillation vials. Trap I is a 300 ml stainless-steel sample cylinder filled with 0.3 mm dia. activated coconut charcoal. Trap II is a 70 cm length of 1.9 cm O.D. stainless steel pipe filled with 3 mm dia. titanium sponge. Trap III is a 345 cm length of 0.95 cm O.D. copper tubing filled with 0.3 mm dia. activated coconut charcoal. Trap IV is a 15 cm length of 0.5 cm O.D. copper tubing filled with 0.3 mm dia. activated coconut charcoal.

The ^{83m}Kr generator (Figure 1) is contained in a 6 cm length of 0.9 cm (O.D.) copper tubing capped at one end. ^{83m}Kr (1.86 h half-life) is the daughter of ^{83}Rb (83 d half life). Two ml of a ^{84}Rb solution containing approximately 0.1 mCi ^{83}Rb, which has gone through several half-lives, is evaporated to dryness in the generator container. The container is plugged with cotton to prevent the escape of rubidium salt particles during the equilibration procedure.

The ^{83m}Kr generator, the reference volume (V_r) and the spiking volume (V_p) are all under vacuum, and at equilibrium the activity in V_p can be calculated from the activity in V_r knowing the ratio of the two volumes. The purity of the ^{83m}Kr gas is checked by determining its half-life in V_r.

Experimental results have shown that the most accurate way to introduce the ^{83m} Kr spike into the system is to mix the spike with the air sample. Krypton recoveries range from 80 to 90 percent at an average of 86 percent.

Reagents

Liquid scintillation cocktail [7.5 g of 2,5-diphenyloxazole (PPO) and 1.5 g of p-Bis (o-methylstyryl) benzene (bis-MSB) per liter of p-xylene]. Reflux for approximately 15 minutes before using to remove dissolved oxygen.

Procedure--Spiking Air Samples with ^{83m}Kr (Figure 1)

Transfer approximately one cubic meter of air from compressed gas cylinder to balloon. The volume may be approximated by measuring the circumference of the balloon.

1. The ^{83m}Kr generator will have to be prepared by evacuating to a pressure of 5 microns or less at least 24 hours before the generator can be used. Evacuation will remove the ^{83m}Kr that has been formed and it will take about 24 hours to regenerate.

To prepare the generator, close valves A, 1, 6, and 7, then open valves 2, 3, 4, and 5 to vacuum pump number 1. When the evacuation is completed, close valves 2, 3, 4, and 5. This operation should only be necessary again whenever the system is not operated over an extended period of time. Open valves A, 1, 3, 4, and 5 and evacuate to a pressure of less than five microns of mercury. Close valves 4 and 5, open valve 2, and allow the ^{83m}Kr to equilibrate for about ten minutes.

2. Close valves 2, 1, A, and 3. Open valves 11, 8, 7, 4, and 6 and start sample flow.
3. Remove liquid scintillation vial (V_r) along with valve A and fill with liquid scintillation solution. (See Note 1 and Note 2.) Agitate gently to dissolve krypton in mix.
4. After the sample and spike have been transferred to the balloon, stop the sample flow and close valves 11, 8, 7, 4, and 6. The sample is now ready for introduction into the krypton separation system.

Procedure--Separating Krypton From the Other Air Constituents (Figure 2)

5. Cool trap I with liquid nitrogen (LN) 30 minutes before passing sample through. Start the spiked sample through trap I by opening valves 33, 34, 32, 30, 28, 9, and 11. Adjust the flow rate with needle valve C (approximately ten liters/min.). Continue adding liquid nitrogen to trap I. While sample is passing through trap I, perform steps 7-10.
6. Measure the volume of air passing through trap I with a wet test meter that is connected to the exhaust vent of vacuum pump 2 .
7. To clean trap III, open valves 41, 42, 44, 45, and 47 and heat with a wrap-around furnace for about an hour at 350°C. Remove the heat and close valves 41, 42, 45, and 47. Before opening the helium valve, let trap III cool for approximately 10 minutes.

8. Open valves 43 and 44. When the helium flow into trap III stops, close valves 43 and 44. After trap III cools, a partial vacuum is formed. After cleaning trap III, the large pump is available for cleaning trap IV.
9. To clean trap IV, open valves 21 and 20, and heat with a heat gun for about 15 minutes. Remove the heat gun and close valves 20 and 21. Open valves 43, 16, 15, and 13. After a few seconds, close valve 17 and open valve 18. When the helium flow into trap IV stops, close valves, 18, 16, and 43.
10. About ten minutes before the spiked air sample has completely passed through trap I, open valves 43, 42, 26, 25, 12, and 13 to start the helium flow through the thermal conductivity cell (TCC). Adjust the helium flow rate (approximately 3 liters/min.) with needle valve D. With the helium flow rate adjusted, switch on the TCC recorder and set recorder baseline. Then close valves 13, 12, 25, 26, 42, and 43.
11. After all the spiked sample has been removed from the balloon, close valves 11 and 9 and warm the precooler with a heat gun. Then close valves 28, 30, and 33. Open valves 31, 24, 12, and 13. Adjust the helium flow to three liters per minute with valve D. Remove LN from trap I and replace with a dry ice-acetone slush. Continue purging for one hour with helium flowing through trap I. Cut off vacuum pump 2.
12. While trap I is being purged, open valves 41 and 40 and heat trap II to 900°C. After several minutes, close valves 40 and 41 but continue heating. Evacuate V_s to less than 5 microns of mercury by opening valves 21, 22, 23, and B. Cool trap III with LN for 20 minutes.
13. When the TCC reading returns to near the baseline setting, adjust the helium flow to one liter per minute. Close valves 12 and 13 and open valves 26, 25, 12, 15, 16, 40, 44, 45, and 46. Remove the dry ice-acetone Dewar from trap I and replace with an

electric wrap-around furnace and heat to 350°C to transfer the gases remaining in trap I to trap III. After about 20 minutes, close valves 46, 16, 15, 12, and 31.

14. Shut off the furnace to trap II and open valves 38, 36, and 35. After about a minute close valve 35 and 36. Continue heating trap I for about an hour at 350°C making sure that it is being evacuated by vacuum pump 2. Later, close connection to pump 2 and connect to vacuum pump 1.
15. Cool trap IV with LN and open valves 43, 44, 45, 27, 25, 12, 15, and 17. Adjust the helium flow to about 100 ml /min. Remove LN from trap III and replace with an ice water bath. Follow the TCC response and about a minute before the krypton appears close valve 17 and open valves 18 and 19. After the krypton has been transferred from trap III to trap IV, close valves 19, 18, 15, 12, 25, 27, 45, 44, and 43. Turn off the TCC recorder.
16. To remove the excess helium from trap IV close valve 22, open valves 20 and 21 and evacuate to less than 5 microns of mercury. Close valve 21 and open valves 22, 23 and B. Remove LN from trap IV and cool scintillation vial V_s with the LN. Heat trap IV with heat gun for five minutes. Close valves B, 23, and 20. Remove LN from the scintillation vial and warm to room temperature. Remove the scintillation vial along with valve B and fill with liquid scintillation solution. The time required to this point is about four hours.
17. Count V_r and V_s for ^{83m}Kr to determine chemical recovery. After the ^{83m}Kr has decayed, count V_s for ^{85}Kr.

Calculations

Calculate chemical yield using the following equation:

$$\text{chemical yield} = \frac{V_r(\text{cpm})}{V_s(\text{cpm})} .$$

Since data are reported at standard temperature and pressure, volume corrections must be made. From the gas law, $pV = RT$, R is constant. Therefore,

$$V_2 = V_1 \left[\frac{T_2}{T_1}\right]\left[\frac{P_1}{P_2}\right],$$

where

V_2 = volume at STP,
V_1 = measured volume in liters (from wet test meter),
T_2 = standard temperature 273°K,
T_1 = sample temperature °C + 273,
P_1 = measured pressure in mm of Hg, and
P_2 = standard pressure, 760 mm of Hg.

Then

$$^{85}\text{Kr pCi/liter of air at STP} = \frac{C_1 - C_B}{(2.22)(E)(R)(V)}$$

where

C_1 = beta counts per minute,
C_B = background counts per minute,
E = counter efficiency,
V = volume of air (liters),
R = fractional yield based on ^{83m}Kr, and
2.22 = dpm/pCi.

Calculate the lower limit of detection (LLD) of krypton-85 in picocuries per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(V)(T)}$$

where

E = counter efficiency,
R = fractional yield,
V = volume of air (liters),
2.22 = dpm/pCi, and
T = counting time.

Notes

1. To clean scintillation vials, pump approximately 10 ml of acetone into the vials using a 20-ml syringe fitted with a female adapter. Expel acetone into same syringe. Repeat two more times. Evacuate vials until dry; then heat in oven at 100°C. Store in a desiccator until ready for use.
2. After injecting vials with ^{83m}Kr spike or sample, fill with cooled refluxed scintillation mix using a 20-ml syringe fitted with a female Luer adapter.
3. A background count is obtained for each vial filled with scintillation solution.

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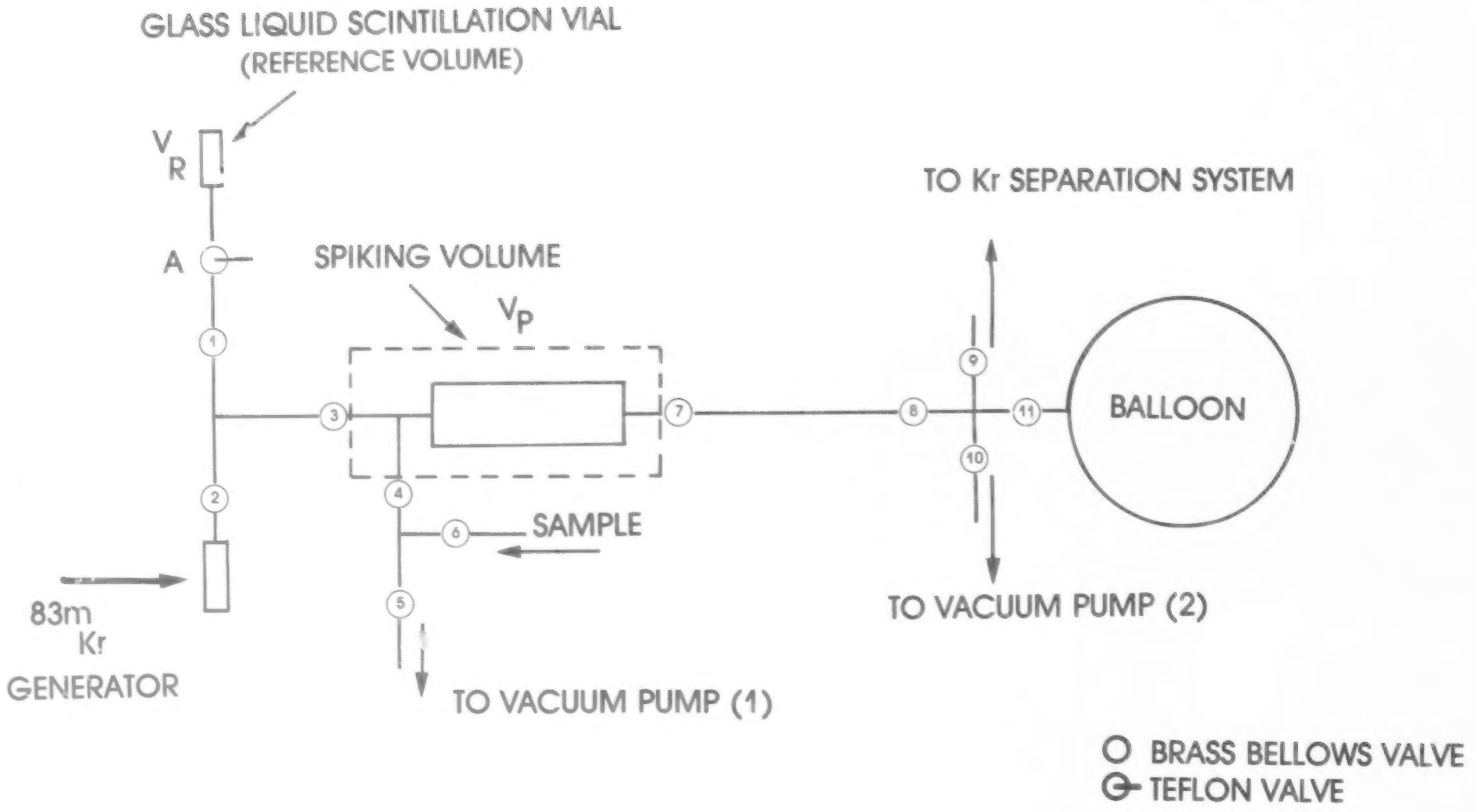
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TO VACUUM PUMP (1)
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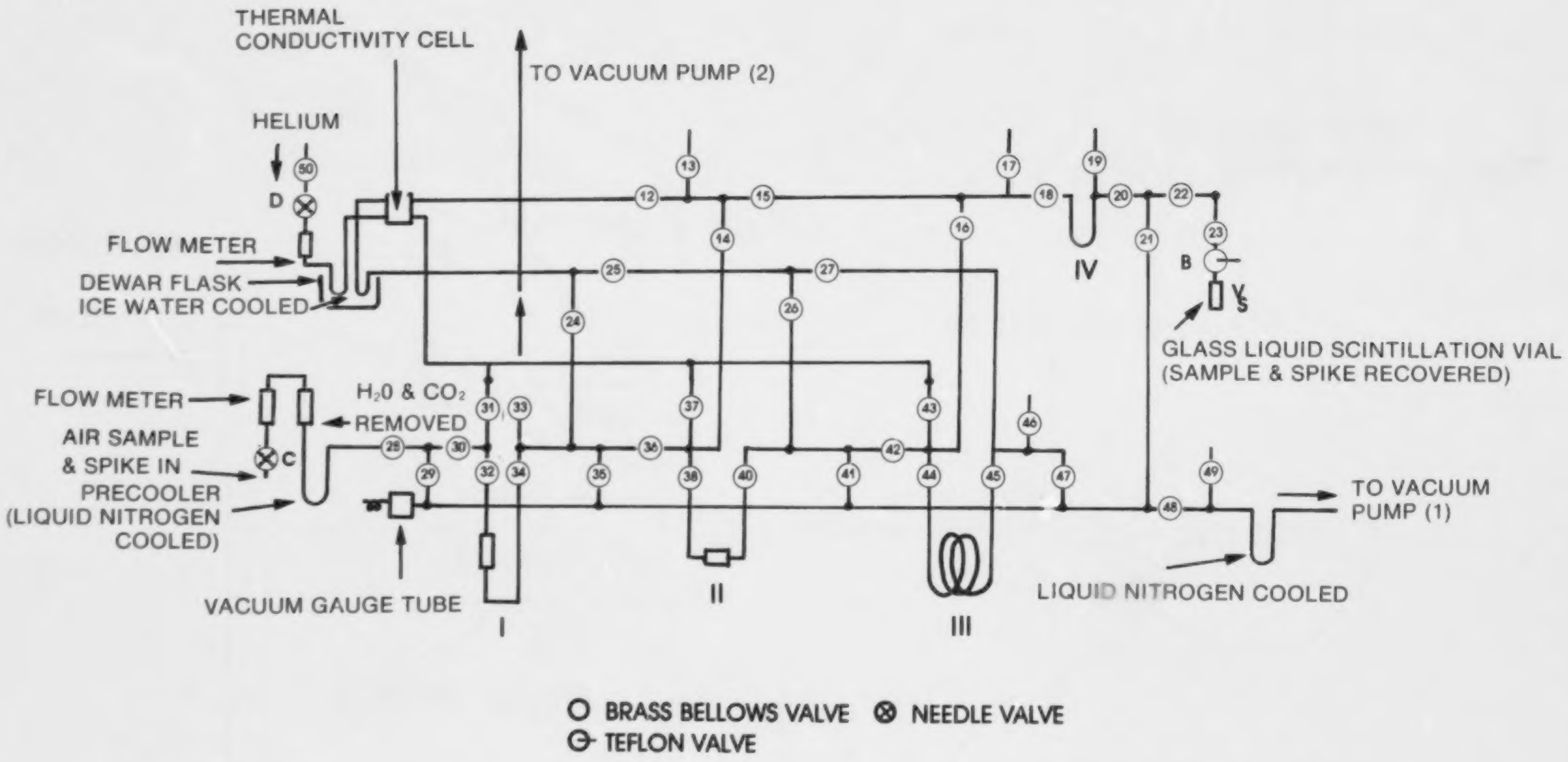
BALLOON
TO VACUUM PUMP (2)
O BRASS BELLOWS VALVE
TEFLON VALVE

Figure 1. Air spiking system.


THERMAL CONDUCTIVITY CELL
TO VACUUM PUMP (2)
HELIUM
D
FLOW METER
DEWAR FLASK
ICE WATER COOLED
FLOW METER
H₂0 & CO₂ REMOVED
AIR SAMPLE & SPIKE IN
C
PRECOOLER (LIQUID NITROGEN COOLED)
VACUUM GAUGE TUBE
I
II
III
IV
B
V
S
GLASS LIQUID SCINTILLATION VIAL (SAMPLE & SPIKE RECOVERED)
TO VACUUM PUMP (1)
LIQUID NITROGEN COOLED
12
13
14
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O BRASS BELLOWS VALVE
⊗ NEEDLE VALVE
TEFLON VALVE

Figure 2. Krypton separation system.

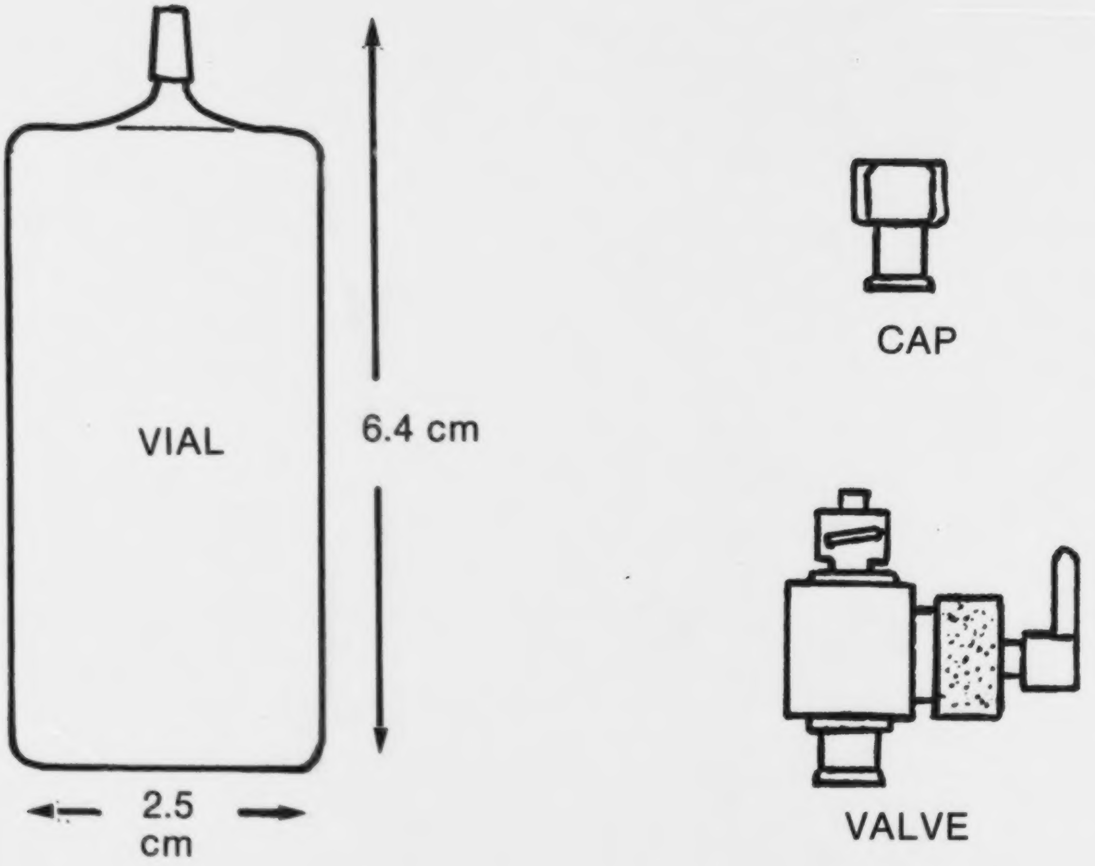
VIAL
6.4 cm
2.5 cm
CAP
VALVE

Figure 3. Scintillation vial assembly.

RADIOCHEMICAL DETERMINATION OF PHOSPHORUS-32 IN FISH MUSCLE

Principle

The fish muscle is dried and ashed at 550°C. After wet oxidation, the ash is solubilized and filtered. The phosphorus is decontaminated by passing the solution over anion and cation resins. Phosphorus is precipitated as magnesium ammonium phosphate, which is then filtered, dried to a constant weight, and weighed. The precipitate is suspended in a liquid scintillation solution for radioassay. Aliquots of the solution are removed for stable phosphorus analysis to determine chemical yield.

Apparatus

1. Glass fiber filters, 47 mm.
2. Ion exchange columns. Anion 2 cm internal diameter, 10.5 cm L; cation 2.7 cm internal diameter, 17 cm L.
3. Liquid scintillation spectrometer.
4. Liquid scintillation vials.
5. Spectrophotometer and accessories.
6. Suction filter apparatus for 47 mm filters.

Column Preparation

Anion column: 25 ml of Dowex-1 (50-100 mesh).
Charge with 100 ml 6M HCl at a flow rate of 5 ml/minute.

Cation column: 75 ml Dowex-50W X 8 (50-100 mesh).
Charge with 250 ml 1M HCl at a flow rate of 5 to 10 ml/minute.
Rinse with 250 ml distilled H_2O.

Reagents

1. Ammonium chloride, crystalline reagent.
2. Ammonium hydroxide, 15M, NH_4OH reagent.

3. Ammonium hydroxide, 1M. Dilute 67 ml of the NH_4OH reagent to 1 liter with distilled water.
4. Ammonium hydroxide, 0.1M. Dilute 6.7 ml of the NH_4OH reagent to 1 liter with distilled water.
5. Ethanol, 95 percent reagent.
6. Hydrochloric acid, 12M, 37 percent HCl reagent.
7. Hydrochloric acid, 6M. Dilute 500 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
8. Hydrochloric acid, 0.1M. Dilute 8.3 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
9. Magnesia mixture. Dissolve 55 g $MgCl_2 \bullet 6H_2O$ in a minimum amount of water. Add 140 g NH_4Cl and 350 ml 15M NH_4OH. Dilute to 1 liter. Let stand 1 hour, filter, and store in glass bottle.
10. Magnesium chloride. Reagent grade $MgCl_2 \bullet 6H_2O$.
11. Nitric acid, 16M, 70 percent HNO_3 reagent.
12. Oxidation mixture, 10 parts HNO_3: 1 part $HClO_4$: 4 parts H_2SO_4.
13. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
14. Scintillation solution. Aqua Sol or equivalent. See Note 1.
15. Sulfuric acid, 18M, 96 percent H_2SO_4 reagent.

Procedure

1. Dry up to 450 g fish muscle in a ceramic dish at 200°C for 12 hours. Slowly increase temperature to 400°C for a few hours. Remove and grind ash to uniformity. Increase temperature to 550°C and ash for 24 to 48 hours.
2. Transfer ash to a 400 ml beaker. Dissolve the residue in ceramic dish with two 15 ml portions of 16M HNO_3 and add rinses to beaker containing ash.
3. Evaporate to 25 ml or until a frothy brown residue is obtained.

4. In a perchloric acid fume hood, add 20 ml of the oxidation reagent and evaporate on a hot plate. (After the HNO_3 has evaporated, dense white $HClO_4$ fumes appear and the solution changes to a white slurry. Continue evaporating until all the H_2SO_4 has evaporated and the slurry changes to a shiny white residue).
5. Dissolve the residue in 20 ml 6M HCl. Warm on a hot plate. Stir with a glass rod to dissolve all the residue. Evaporate to near dryness. Add 40 ml 6M HCl and raise temperature to boiling while stirring.
6. Filter the hot solution through a 47 mm glass fiber filter and discard the filter with residue.
7. Dilute the filtrate to exactly 50 ml with 6M HCl. Remove two 0.5 ml portions for stable phosphorus determination.
8. Transfer the 49 ml solution to an anion exchange column. Rinse sample container with a few ml of 6M HCl and add to column. Pass sample through at 5 ml/minute. Collect in 300 ml beaker.
9. Elute column with two 75 ml portions of 6M HCl. Collect all fractions. (If interested in Fe determination, elute Fe with 100 ml 0.1M HCl, followed by 25 ml H_2O).
10. Evaporate column effluents to near dryness. When salts begin to form ($\cong$ 50 ml volume) turn heat to low to prevent bumping.
11. Dissolve the residue in 50 ml of 0.1M HCl by heating and stirring. Raise the temperature to boiling. Filter through glass fiber filter and discard filter with residue.
12. Pass sample through cation exchange column at 5-10 ml/minute. Elute column with two 75 ml aliquots of H_2O. Collect the effluents and evaporate to 100 ml volume. Take two 0.5 ml samples for stable phosphorus yield measurement.
13. Precipitate the phosphorus as $MgNH_4PO_4$ by adding 100 ml of magnesia mixture. Cool in an ice bath. Add a few more ml magnesia mixture to check completeness of precipitation.

14. Filter and collect precipitate on 47 mm glass fiber filter. Wash successively with 0.1M NH_4OH and ethanol. Place filter paper in tared Coors crucible.
15. Dry in 100-120°C oven for one hour. Cool, weigh, then place filter paper and precipitate in a glass scintillation vial. This will nearly fill the vial; then add scintillation solution, a little at a time, until the precipitate is suspended and the vial is full (shoulder of vial).
16. Count in liquid scintillation counter for desired amount of time.

Calculations

Calculate the concentration, Z, of phosphorus-32 in picocuries per gram as follows:

$$Z = \frac{C_1 - C_B}{(2.22(E)(Y)(W)(D)}$$

where

C_1 = sample count rate,

C_B = background count rate,

E = counting efficiency (cpm/dpm),

Y = chemical yield - colorimetric analyses of phosphorus in the aliquots of steps 7 and 12, if no loss occurs in later steps,

W = weight of fish sample in grams,

D = decay factor = $e^{\frac{-0.693(d)}{14.3}}$ when d = days between sample collection and phosphorus-32 counting, and

2.22 = dpm/pCi

Calculate the lower limit of detection (LLD) of phosphorus-32 in picocuries per gram as follows:

$$\text{LLD} = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(Y)(W)(D)(T)}$$

where

C_B = background count rate,
T = counting time,
E = counting efficiency,
Y = chemical yield,
W = weight of fish (grams),
D = decay factor = $e^{\frac{-0.693(d)}{14.3}}$ when d = days between sample collection and phosphorus-32 counting, and
2.22 = dpm/pCi.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

Notes

1. Aqua Sol is a product of New England Nuclear Corp., Boston, MA.

References

1. Krieger, H.L., and Gold, S. Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions. EPA-R4-73-014, National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio (May 1973).

COLORIMETRIC DETERMINATION OF STABLE PHOSPHORUS IN BIOLOGICAL SAMPLES

Principle

An aliquot of dissolved ash is evaporated to fumes of perchloric acid to remove fluoride and reducing agents. Ammonium vanadate and ammonium molybdate are added and a yellow molybdovanadophosphoric acid complex is formed which obeys Beer's law. The intensity of the yellow complex is measured with a colorimeter at a wave length of 400 nm. The phosphorus content of the sample is determined by comparison of its absorbance with that of a series of phosphorus standards.

Special Apparatus

1. Colorimeter or spectrophotometer, operable at 400 nm.
2. Absorption cells, 1 cm light path.
3. Glassware.

Reagents

1. Ammonium molybdate, 0.16M Mo. Dissolve 28.1 g reagent grade $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ in distilled water and dilute to 1 liter.
2. Ammonium vanadate, 0.02M V. Dissolve 1.17 g reagent grade NH_4VO_3 in a mixture of 17 ml 12M $HClO_4$ and 400 ml distilled water and dilute to 500 ml.
3. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
4. Sodium chloride. NaCl reagent crystals.
5. Standard phosphorus solution, 0.1 mg P/ml. Dissolve 0.439 g KH_2PO_4 in distilled water and dilute to 1 liter.

Procedure

1. Pipet an aliquot of dissolved ash which contains 0.1- 1.0 mg of phosphorus into a 150 ml beaker. Add 5.0 ml of 12M perchloric acid and evaporate to dense white fumes on a hot plate. See Note 1.

2. Cool the solution and transfer with H_2O to a 100 ml volumetric flask. Add 10.0 ml of NH_4VO_3 solution and 25.0 ml of $(NH_4)_6Mo_7O_{24}$ solution. Dilute to volume and mix well.
3. Set the colorimeter or spectrophotometer at a wave length of 400 nm and measure the cell blanks with a reagent blank prepared in the same manner as the sample. See Note 2.
4. Measure the absorbance (A_s) of the sample against the reagent blank.
5. Carry 1.0, 2.0, 3.0,, 5.0, and 10.0 ml aliquots of the standard phosphorus solution through the procedure. Calculate an absorbance index (a_s) for each aliquot by dividing its absorbance by the weight of phosphorus in milligrams. The average of these absorbance indices is used to calculate the phosphorus content of the sample. See Note 3.

Calculations

Calculate the concentration, Z, of phosphorus in the sample in grams per kilogram as follows:

$$Z = \frac{(A - B)(C)(D)}{(E)(F)(G)(H)(1000)}$$

where

A = absorbance (A_s),
B = cell blank,
C = sample volume in liters,
D = weight of total ash,
E = absorbance index (a_s),
F = sample aliquot in liters,
G = weight of ash dissolved in grams, and
H = weight of sample in kilograms.

Notes

1. If the sample is suspected to contain dichromate, 1 gram of NaCl is added to the solution in Step 1. If red fumes of chromyl chloride appear, rinse down the sides of the beaker and evaporate to fumes again. Repeat until fumes of chromyl chloride are no longer observed. Continue the procedure with Step 2.
2. The slit width is adjusted so that the reagent blank reads 100 percent transmission. The cell blanks are determined by filling each cell with the reagent blank and measuring its relative absorbance. The cell with the lowest blank is used as a reference cell when measuring the absorbance of the sample.
3. At least three standards should be run with each set of samples and an absorbance index calculated. This should be used to calculate the phosphorus content of samples.

References

1. Cee, A. and Deitz, V. R., "Determination of Phosphate by Differential Spectrophotometry," Analytical Chemistry 25, 1320 (1953).
2. Quinlan, K. P., and DeSesa, M. A., "Spectrophotometric Determination of Phosphorus by Molybdovanadophosphoric Acid," Analytical Chemistry 27, (1955).

RADIOCHEMICAL DETERMINATION OF LEAD-210
IN WATER AND SOLID SAMPLES

Principle

Bismuth and lead carriers are added to a measured sample aliquot. The lead is separated as a lead bromide complex by solvent extraction with Aliquat 336 in toluene. Bismuth is separated from the lead as bismuth oxychloride and bismuth-210 is measured in a low-background beta counter after suitable ingrowth. The chemical recovery of lead is measured using an atomic absorption spectrophotometer. Bismuth recovery is measured gravimetrically.

Special Apparatus

1. Atomic absorption spectrophotometer with lead lamp.
2. Separatory funnels, 250 ml capacity.
3. Combination magnetic stirrer and hot plate.
4. Low background beta counter with 7 mg/cm^2 window.
5. Centrifuge, table model.
6. Suction filter apparatus.
7. Filter paper, Whatman 42 or equivalent, 55 mm dia. cut to fit 47 mm suction filter apparatus.

Reagents

1. Aliquat 336, methyltricaprylammonium chloride, General Mills Chemical Co.
2. Aliquat 336, 30 percent in toluene. Mix 300 ml of Aliquat 336 with 700 ml of toluene. Just prior to use, wash solution twice with equal volume of 1.5 M HBr.
3. Ammonium hydroxide, 15 M.
4. Bixmuth carrier, 10 mg.Bi^{+2}/ml. Dissolve 23.2 g $Bi(NO_3)_2 \cdot 5H_2O$ in 0.8 M HNO_3 and dilute to 1 liter with 0.8 M HNO_3.
5. Ethanol, 95 percent reagent.

6. Hydrobromic acid, 9 M. 48 percent HBr reagent.
7. Hydrobromic acid, 3 M. Dilute 333 ml of the 48 percent HBr to 1 liter with distilled water.
8. Hydrobromic acid, 1.5 M. Dilute 167 ml of the 48 percent HBr to 1 liter with distilled water.
9. Hydrobromic acid, 0.1 M. Dilute 11 ml of the 48 percent HBr to 1 liter with distilled water.
10. Hydrochloric acid, 12 M. 37 percent HCl reagent.
11. Hydrochloric acid, 8 M. Dilute 667 ml of the 37 percent HCl reagent to 1 liter with distilled water.
12. Hydrogen peroxide, 50 percent H_2O_2 reagent.
13. Lead carrier, 20 mg Pb^{+2}/ml. Dissolve 32.0 g lead nitrate in 0.8 M HNO_3 and dilute to 1 liter with 0.8 M HNO_3.
14. Lead standard solution, 1000 ppm Pb. Commercially available certified standard.
15. Nitric acid, 16 M. 71 percent HNO_3 reagent.
16. Nitric acid, 0.8 M. Dilute 50 ml of the 71 percent HNO_3 reagent to 1 liter with distilled water.
17. Perchloric acid, 12 M, 70 percent $HClO_4$ reagent.
18. Toluene, reagent grade.

Sample Preparation (solid sample)

1. Add 1 ml lead carrier to weighed aliquot of sample in beaker.
2. Add 50 ml 16 M HNO_3 and 5 ml 50 percent H_2O_2 and digest until sample has dissolved.
3. Evaporate sample just to dryness and add 100 ml 3 M HBr and cool to room temperature.

Sample Preparation (water sample)

1. Add 1 ml lead carrier and 5 ml 16 M HNO_3 to a liter water sample. Evaporate to about 100 ml.
2. Add 100 ml 16 M HNO_3 to sample and evaporate to dryness.

3. Add 25 ml 3 M HBr to sample and evaporate to dryness.
4. Add 100 ml of 3 M HBr to residue, heat to dissolve, and cool to room temperature.

Procedure

1. Transfer the sample in 3 M HBr solution to a 250 ml separatory funnel containing 75 ml of washed Aliquat 336.
2. Shake for 30 seconds. Let separate and discard the aqueous phase.
3. Wash the organic phase three times with 50 ml aliquots of 0.1 M HBr and discard all washes.
4. Strip the lead from the organic phase by shaking twice for 30 seconds with 50 ml aliquots of 12 M HCl.
5. Combine the strip solutions in a 400 ml beaker and add 100 ml of 16 M HNO_3.
6. Evaporate the solution just to dryness.
7. Add 5 ml of 8 M HCl and 5 ml of 12 M $HClO_4$ to the residue from step 6 and heat to dryness.
8. Add 10 ml of 16 M HNO_3 to the sample and heat to dryness.
9. Add 10 ml of 12 M HCl to the sample and heat to dryness.
10. Add 10 ml of 16 M HNO_3 and 10 ml of 12 M HCl and heat until volume is reduced to approximately 10 ml.

First Milking

1. Add 1 ml of bismuth carrier to sample and transfer to a 40 ml centrifuge tube with a distilled water rinse.
2. Adjust pH of sample to 8 with 15 M NH_4OH.
3. Heat the sample with stirring in a hot water bath.
4. Cool and centrifuge. Discard the supernate.
5. Dissolve the precipitate by first suspending in 5 drops of 12 M HCl. Add 5 to 10 ml of distilled water to dissolve the precipitate.
6. Add 40 ml water and heat with constant stirring.

7. Cool, centrifuge, and reserve the supernate in a 250 ml beaker.
8. Repeat steps 5 through 7 twice more, combining the supernates. Discard the precipitate, record the time and date for ingrowth of bismuth-210. See Note 1.
9. Add 1 ml of bismuth carrier and 3 to 5 ml of 12 M HCl to the combined supernates. Reduce the volume to less than 100 ml.
10. Cool, transfer to a 100 ml volumetric flask and bring to volume.
11. Dilute 1 ml of sample to 10 ml in a 10 ml volumetric flask.
12. Determine the recovery of lead carrier by measuring the sample in the 10 ml volumetric flask on an atomic absorption spectrophotometer at 283 nm. See Note 2.
13. Allow 2 to 3 weeks for ingrowth of bismuth-210 into the main portion of the sample (step 10).

Second Milking

1. Transfer the solution from the 100 ml volumetric flask to a 250 ml beaker and evaporate to about 15 ml.
2. Transfer to a 40 ml centrifuge tube and adjust the pH to 8 with 15 M NH_4OH. Centrifuge and discard the supernate.
3. Dissolve the precipitate by suspending in 5 drops of 12 M HCl and adding 5 to 10 ml H_2O. Bring volume of sample to 40 ml with water. Record the time and date for decay of bismuth-210.
4. Heat with constant stirring in a hot water bath. Cool and centrifuge. Reserve the supernate for additional lead-210 analysis.
5. Dissolve the precipitate by first suspending in 5 drops of 12 M HCl. Add 5 to 10 ml of water to complete solution. Dilute the sample to 40 ml with water.
6. Heat in a hot water bath with constant stirring. Cool and centrifuge. Combine the supernate with that from step 4.
7. Dissolve the precipitate as in step 5 and dilute with 40 ml of water.

8. Heat in a hot water bath with constant stirring. Cool, filter with suction on a weighed 2.5 cm filter membrane.
9. Wash the precipitate with water and ethanol and dry the precipitate for 30 minutes at 110°C.
10. Cool and weigh the precipitate.
11. Count the sample using a low background beta counter with a 7 mg/cm^2 window. Record the time and date for decay of bismuth-210.
12. Standardize the counter with a known amount of lead-210 from which bismuth-210 has been separated and prepared in the same way as the sample.

Calculations

Calculate the concentration, Z, of lead-210 in picocuries per milliliter or gram as follows:

$$Z = \frac{(C)}{(2.22)(E)(A)(P)(B)(I)(D)}$$

where

C = cpm (net),
E = eff,
A = amount of sample (ml or g),
P = chemical yield of lead (determined by AA),
B = chemical yield of bismuth (determined gravimetrically by weight of BiOCl),
I = ingrowth of Bi^{210} (time from 1st milking to 2nd milking),
D = decay of Bi^{210} (time of separation 2nd milking in step 3 to midpoint of counting time), and
2.22 = dpm/pCi.

Calculate the lower limit of detection (LLD) for lead-210 in picocuries per milliliter or gram as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(A)(P)(B)(I)(D)(T)}$$

where

C_B = background count rate (c/m),
T = counting time (minutes),
E = counter efficiency,
2.22 = dpm/pCi,
P = chemical yield of lead (AA determination),
B = chemical yield of bismuth (gravimetric),
I = ingrowth of bismuth-210,
D = decay of bismuth-210, and
A = amount of sample (ml or g).

Notes

1. If the need arises for a fast indication of the amount of lead-210 in a sample, the precipitate in step 8 of the first milking can be saved on a tared filter and counted for bismuth-210. If the sample in question has been collected for over 21 days, the results are compatible with final results.
2. The calibration curve should have a working range of 0 to 50 ppm.

References

1. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.
2. Petrow, H.G., and Cover A., "Direct Radiochemical Determination of Lead-210 in Bone," Analytical Chemistry 37, 1659 (1965).

RADIOCHEMICAL DETERMINATION OF PROMETHIUM-147
IN AQUEOUS AND URINE SAMPLES

Principle

Neodymium carrier is added to a measured sample aliquot. The rare earths are separated by passing the sample over anion exchange resin. Promethium-147 is precipitated with the rare earth carrier as an oxalate. After wet ashing, the oxalate is reprecipitated and dissolved in EDTA. The solution is mixed with a liquid scintillation solution and the promethium-147 is radioassayed in a liquid scintillation counter.

Special Apparatus

1. Liquid scintillation counter at ambient temperature operation. See Note 1.
2. Low background counting vials, 25 ml capacity. See Note 2.
3. Ion exchange columns 3.2 cm I.D., 17 cm length.
4. Centrifuge.
5. Filter membrane, Millipore HAWP, 25 mm dia. or equivalent. See Note 3.
6. Suction filter apparatus for 25 mm filter membrane.

Reagents

1. Ammonium hydroxide, 15 M. NH_4OH reagent.
2. Anion exchange resin. Dowex 1 X 8 or equivalent, 100-200 mesh, chloride form.
3. Aqua regia. Four parts 12 M HCl; one part 15 M HNO_3 by volume. Prepare immediately before use.
4. p-Bis (o-methylstyryl) benzene (bis MSB).
5. Citric acid, crystalline reagent.
6. Citric acid, 1 M pH 4.5. Dissolve 192 g citric acid in 750 ml distilled water and adjust to pH 4.5 with careful addition of 15 M NH_4OH using pH meter. Dilute to 1 liter with distilled water.

7. Citric acid, .01 M. Dilute 5 ml of the 1 M citric acid solution to 500 ml with distilled water.
8. 2,5-Diphenyloxazole (PPO).
9. Disodium ethylenediamine tetraacetic acid, 9 percent. Dissolve 90 grams reagent grade Na_2EDTA in 800 ml distilled water and dilute to 1 liter.
10. Ethanol, 95 percent reagent.
11. Hydrochloric acid, 12 M. 37 percent HCl reagent.
12. Hydrochloric acid, 3 M. Dilute 250 ml of the 37 percent HCl reagent to 1 liter with distilled water.
13. Neodymium carrier, 10 mg Nd^{+3}/ml. Dissolve 23.3 g high purity Nd_2O_3 in 83 ml 12 M HCl and dilute to 1 liter with distilled water. Standardize by preparing neodymium oxalate precipitates for weighing.
14. Nitric acid, 15 M. 70 percent HNO_3 reagent.
15. Oxalic acid, 1 M. Dissolve 126 g $H_2C_2O_4 \cdot 2H_2O$ in 700 ml distilled water and dilute to 1 liter with distilled water.
16. Scintillation solution. Dissolve 7.0 g of 2,5-diphenyloxazole (PPO) and 1.5 g of p-bis (o-methylstyryl) benzene (bis MSB) in 1 liter of p-xylene. Mix this solution with Triton N101 in a volume ratio of 2.75 parts of p-xylene solution to 1 part of Triton N101. The correct volume of Triton N101 is 364 ml for each liter of p-xylene. Store the solution in a brown bottle and protect from sunlight.
17. Triton N101, Rohm and Haas Co., Philadelphia, PA. See Note 4.
18. p-Xylene, scintillation grade reagent.

Procedure

1. Add 1 ml of the neodymium carrier to 10 ml of 1 M citric acid.
2. Add the above mixture to 1 liter of water sample or to 1 liter of filtered urine with stirring. Adjust pH of sample to 4.5.

3. Slurry 100 ml of anion exchange resin with water and add to column. Wash resin with 400 ml 3 M HCl.
4. Replace acid on column with distilled water until pH of eluate is greater than 4.
5. Charge column with 200 ml 1 M citric acid, pH 4.5.
6. Wash column with 200 ml 0.01 M citric acid.
7. Pass urine or water sample through column at a flow rate of 10 ml/minute.
8. Pass 200 ml of 0.01 M citric acid through column at a flow rate of 10 ml/minute.
9. Pass 400 ml of 3 M HCl through column. Begin with a flow rate of 2 to 3 ml per minute. Discard first 30 ml of effluent and collect next 150 ml in a 250 ml centrifuge bottle. Remainder of acid can flow through more rapidly and can be discarded.
10. Replace acid on column with water until pH of eluate is greater than 4. Column is ready for next sample beginning with step 5.
11. Add 5 ml 1 M oxalic acid to the 150 ml of column eluate in the centrifuge bottle.
12. Adjust pH to 1.7 using 15 M NH_4OH with stirring.
13. Cool contents of centrifuge bottle in an ice bath for 30 minutes and centrifuge.
14. Discard supernate and transfer precipitate to a 40 ml centrifuge tube and centrifuge. Discard supernate.
15. Wash precipitate with 5 ml water and centrifuge.
16. Transfer precipitate to a 100 ml beaker using distilled water.
17. Evaporate contents of beaker just to dryness and add 10 ml of aqua regia.
18. Evaporate sample to dryness and repeat steps 17 and 18.
19. Add 10 ml 3 M HCl to beaker and stir to dissolve residue.
20. Transfer contents to a 40 ml centrifuge tube, washing beaker with 3 M HCl, bringing volume in tube to approximately 30 ml.

21. Add 2 ml 1 M oxalic acid to centrifuge tube and adjust pH to 1.7 using 15 M NH_4OH.
22. Cool contents in ice bath for 30 minutes and centrifuge. Discard supernate.
23. Wash precipitate with 5 ml distilled water and centrifuge. Discard supernate.
24. Filter precipitate on weighed filter membrane.
25. Wash precipitate with 10 ml each of water and ethanol.
26. Allow precipitate to dry in desiccator and weigh.
27. Transfer precipitate and filter membrane to 50 ml beaker.
28. Add 5 ml 9 percent disodium EDTA to beaker. Heat gently to dissolve precipitate.
29. Transfer solution to scintillation vial, washing beaker with 5 ml distilled water which is also put into vial.
30. Add 15 ml of scintillation solution and shake vial to mix contents.
31. Place vial in liquid scintillation counter and allow sample to dark adapt for two hours before counting.
32. Count sample for at least 100 minutes. See Note 5.

Calculations

Calculate the concentration, Z, of promethium-147 in picocuries per liter as follows:

$$Z = \frac{(C_1 - C_B)(S)}{(2.22)(E)(V)(W)}$$

where

C_1 = gross counts per minute,
C_B = background counts per minute,
S = standard weight of neodymium oxalate (mg),

2.22 = dpm/pCi,
E = counter efficiency,
V = sample volume (liters), and
W = weight of precipitate (mg).

Calculate the lower limit of detection (LLD) in picocuries per lite as follows:

$$\text{LLD} = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(V)(T)}$$

where

C_B = background counts per minute,
T = counting time,
2.22 = dpm/pCi,
E = counting efficiency,
R = fractional sample recovery, and
V = sample volume (liters).

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. For optimum performance of the scintillation solution, the temperature at which the counting instrument is kept should be between 18 and 25°C.
2. Low potassium glass or plastic vials should be used to minimize background counts. Plastic vials should be resistant to the scintillation solution. The solvent, p-xylene, will migrate through the plastic vials, therefore the samples should be counted no longer than three days after preparation.

3. Millipore is a registered tradename of Millipore Corp., Bedford, MA.
4. Triton N101 is a tradename for a nonylphenol polyethylene glycol ether.
5. Settings on the liquid scintillation counter should be such as to minimize the background count rate. A standard solution of ^{147}Pm should be used to tag at least six neodymium oxalate precipitates as described in this procedure in order to determine counting efficiency of the instrument at the desired setting.

References

1. Ludwick, J. D., "Liquid Scintillation Counting of Promethium-147, Bioassay Procedure," Analytical Chemistry 36, 1104-1106 (1964).

RADIOCHEMICAL DETERMINATION OF PROMETHIUM-147 IN FECES ASH

Rapid Method

Principle

The weighed feces sample is ashed at 550°C for 72 hours. Neodymium carrier is added and the ash is dissolved in acid. The rare earths are precipitated as oxalate, which is dissolved in EDTA and radioassayed by liquid scintillation counting.

Special Apparatus

1. Liquid scintillation counter at ambient temperature operation. See Note 1.
2. Low background counting vials, 25 ml capacity. See Note 2.
3. Filter membranes, Millipore HAWP, 25 mm dia. or equivalent. See Note 3.
4. Suction filter apparatus for 25 mm filter membrane.
5. Centrifuge.

Reagents

1. Ammonium hydroxide, 15 M. NH_4OH reagents.
2. Ammonium oxalate, crystalline reagent.
3. Ammonium oxalate, 0.5 M. Dissolve 62 g $(NH_4)_2C_2O_4$ in 800 ml distilled water with stirring while warming. Dilute to 1 liter with distilled water. Solution should be saturated at room temperature.
4. p-Bis (o-methylstyryl) benzene (bis MSB).
5. 2,5-Diphenyloxazole (PPO).
6. Disodium ethylenediamine tetraacetic acid, 9 percent. Dissolve 90 g reagent grade Na_2 EDTA in 800 ml distilled water and dilute to 1 liter with distilled water.
7. Ethanol, 95 percent reagent.

8. Hydrochloric acid, 12 M. 37 percent HCl reagent.
9. Neodymium carrier, 10 mg Nd^{+3}/ml. Dissolve 23.3 g high purity Nd_2O_3 in 83 ml 12 M HCl and dilute to 1 liter with distilled water. Standardize by preparing neodymium oxalate precipitates for weighing.
10. Scintillation solution. Dissolve 7.0 g of 2,5-diphenyloxazole (PPO) and 1.5 g of p-bis (o-methystyryl) benzene (bis MSB) in 1 liter of p-xylene. Mix this solution with Triton N101 in a volume ratio of 2.75 parts p-xylene solution to 1 part Triton N101. The correct volume of Triton N101 is 364 ml for each liter of p-xylene. Store the solution in a brown bottle and protect from sunlight.
11. Triton N101, Rohm and Haas Co., Philadelphia, PA. See Note 4.
12. p-Xylene, scintillation grade reagent.

Procedure

1. Ash the feces sample at 550° C for 72 hours.
2. Weigh out 1 g cooled ash into a 100 ml beaker.
3. Pipette 1.0 ml neodymium carrier into beaker.
4. Add 5 ml of 12 M HCl and heat to near boiling. Dilute with 30 ml distilled water and heat to boiling.
5. Cool sample to room temperature and centrifuge.
6. Decant supernate into a 1 liter beaker and dilute to 250 ml with distilled water.
7. Adjust pH of solution between 1.4 and 1.7. Add 5 ml 0.5 M ammonium oxalate and stir vigorously for 30 minutes.
8. Filter precipitate through a weighed filter membrane. Wash precipitate with distilled water and ethanol.
9. Dry the precipitate at 100°C and weigh to determine recovery.
10. Dissolve the precipitate in 5 ml 9 percent disodium EDTA and transfer to a scintillation vial using 5 ml distilled water to transfer the solution.

11. Add 15 ml scintillation solution mix and place vial in liquid scintillation counter.
12. Allow vial to dark adapt for two hours before counting. Count sample for 100 minutes.

Calculations

Calculate the concentration, Z, of promethium-147 in picocuries per gram ash as follows:

$$Z = \frac{(C_1 - C_B)(S)}{(2.22)(E)(W)(P)}$$

where

C_1 = gross counts per minute,
C_B = background counts per minute,
S = standard weight of neodymium oxalate (mg),
2.22 = dpm/pCi,
E = counting efficiency,
W = weight of ash (grams), and
P = weight of precipitate (mg).

Calculate the lower limit of detection (LLD) for promethium-147 in picocuries per gram ash as follows:

$$LLD = \frac{4.66 \sqrt{C_B T}}{(2.22)(E)(R)(W)(T)}$$

where

C_B = background counts per minute,
T = counting time,
2.22 = dpm/pCi,

E = counting efficiency,

R = fractional sample recovery, and

W = sample weight (grams).

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. For optimum performance of the scintillation solution, the temperature at which the counting instrument is kept should be between 18 and 25°C.
2. Low potassium glass or plastic vials should be used to minimize background counts. Plastic vials should be resistant to the scintillation solution. The solvent, p-xylene, will migrate through the plastic vials therefore the samples should be counted no longer than three days after preparation.
3. Millipore is a trademark of the Millipore Corp., Bedford, MA.
4. Triton N101 is a tradename for a nonylphenol polyethylene glycol ether.

References

1. Ludwick, J.D., "Liquid Scintillation Counting of Promethium-147, Bioassay Procedure," Analytical Chemistry 36, 1104-1106 (1964).

RADIOCHEMICAL DETERMINATION OF PLUTONIUM IN ASHED SAMPLES, SOIL, COAL, FLY ASH, ORES, VEGETATION, BIOTA AND WATER

Principle

The sample is ashed at 500°C for 72 hours or evaporated to a smaller volume. Plutonium-242 tracer is added to a weighed or measured aliquot. The solid sample is solubilized by treatment with HF, $HClO_4$, and HCl. Plutonium is extracted from an HCl solution of the sample into a triisooctylamine (TIOA) solution in p-xylene. After washing the TIOA with dilute HCl, the plutonium is stripped from the TIOA with dilute HNO_3. The strip solution is wet ashed and the plutonium is coprecipitated with 0.1 mg lanthanum as fluoride. The precipitate is filtered on a Nuclepore membrane and radioassayed by alpha spectroscopy for plutonium.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Planchets, stainless steel, 32 mm diameter.
3. Plastic graduated cylinder, 100 ml capacity.
4. Separatory funnels, 1 liter capacity.
5. Suction filter apparatus for 25 mm membranes.
6. Teflon beakers. See Note 2.
7. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detector, vacuum pump, and chamber.

Reagents

1. Ascorbic acid, reagent.
2. Ethanol, 95 percent reagent.
3. Hydrochloric acid, 12M, 37 percent reagent.
4. Hydrochloric acid, 9M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.

5. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrofluoric acid, 29M, 48 percent reagent.
7. Hydrofluoric acid, 3M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduated cylinder and storage bottle.
8. Hydrogen peroxide, 50 percent reagent grade.
9. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g high purity $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1M HCl.
10. Nickel foil, 15 cm x 1 cm x 0.1 mm.
11. Nitric acid, 16M, 70 percent reagent.
12. Nitric acid, 0.1M. Dilute 6 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
13. Perchloric acid, 12M, 70 percent reagent.
14. Plutonium-242 tracer solution. Approximately 1 pCi per ml accurately calibrated.
15. Triisooctylamine (TIOA), reagent grade. K and K Chemical Div., ICN Pharmaceuticals, Plainview, N.Y.
16. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
17. p-Xylene, reagent grade.

Sample Preparation (ashed sample)

1. Add 1 g of ashed sample to Teflon beaker.
2. Add measured aliquot of plutonium-242 tracer solution.
3. Add 15 ml of 29M HF and evaporate to dryness. Repeat this step two more times to remove silica as SiF_4.
4. Add 5 ml of 12M $HClO_4$ and 5 ml of 9M HCl. Evaporate to dryness. Repeat this step.
5. Add 10 ml of 12M HCl and transfer solution to glass beaker. Evaporate to dryness. Again add 12M HCl and evaporate.
6. Dissolve sample in warm 9M HCl. Increase volume of 9M HCl to 200 ml.

Sample Preparation (water sample)

1. Filter the water sample of 1 to 4 liters through a fluted filter.
2. Add 100 ml of 12M HCl and a measured aliquot of plutonium-242 tracer to the filtrate.
3. Evaporate the sample to a volume of 200 ml and add 200 ml of 12M HCl.

Procedure

1. Add 2 ml 50 percent H_2O_2, heat gently and set aside for 10 minutes. See Note 3.
2. Place 100 ml 10 percent TIOA in a 1 liter separatory funnel. Add 50 ml 9M HCl and shake for one minute to equilibrate.
3. Drain and discard lower aqueous acid layer after clean separation of two phases.
4. Add the aqueous sample to the TIOA in the separatory funnel and shake the funnel vigorously for two minutes. Vent the funnel stopcock to prevent pressure buildup in the funnel.
5. Allow the phases to separate cleanly and draw off the lower aqueous acid phase and discard.
6. Add 50 ml of 9M HCl to the TIOA solution in the separatory funnel and shake for one minute.
7. Allow the phases to separate; withdraw and discard the lower acid phase.
8. Repeat steps 6 and 7.
9. Strip the plutonium from the TIOA solution by adding 100 ml 0.1M HNO_3 to the separatory funnel and shaking the funnel for two minutes.
10. Allow the phases to separate; withdraw and transfer lower acid phase to a clean separatory funnel.
11. Repeat steps 9 and 10 and combine strip solutions in the clean separatory funnel.

12. Add 100 ml p-xylene to the combined strip solution and shake funnel for one minute.
13. Allow phases to separate cleanly; withdraw lower acid layer into a beaker.
14. Evaporate combined acid solution from step 13 to dryness. Do not overheat.
15. Add 10 ml 16$\underline{M}$ HNO_3 to residue and evaporate to dryness. Do not overheat.
16. Add 5 ml 9$\underline{M}$ HCl and 5 ml 12$\underline{M}$ $HClO_4$ to residue and evaporate to dryness.
17. Repeat step 16.
18. Add 10 ml 12$\underline{M}$ HCl and evaporate to dryness.
19. Repeat step 18.
20. Add 50 ml 1$\underline{M}$ HCl to sample and warm gently to dissolve residue.
21. Heat sample solution to 80°C with stirring and add 50 mg ascorbic acid. Do not overheat.
22. Suspend clean nickel metal strip into the solution for two hours to remove polonium.
23. Remove nickel and evaporate the solution to dryness.
24. Add 15 ml 1$\underline{M}$ HCl to sample residue and warm to approximately 50°C.
25. Add 0.5 ml 50 percent H_2O_2, 1 ml of lanthanum carrier and 5 ml of 3$\underline{M}$ HF to precipitate LaF_3 carrying plutonium. Mix well and set aside for 30 minutes.
26. Using suction, filter coprecipitated sample through a filter membrane.
27. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
28. Remove clamp and top of funnel with the suction on. Allow membrane to dry.
29. Mount membrane carefully on a 32 mm diameter planchet using double stick tape.
30. Count sample for 1000 minutes on an alpha spectrometer.

Calculations

Calculate the concentration, Z, of plutonium in picocuries per gram as follows:

$$Z = \frac{(A-A_1)(F)}{(2.22)(B-B_1)(E)(W)(T)}$$

where

A = gross sample counts that appear in the plutonium-238 or plutonium-239 alpha energy region,

A_1 = background counts in the same alpha energy region and time period as A above,

B = gross tracer counts which appear in the alpha energy region of the tracer isotope,

B_1 = background counts in the same alpha energy region and time period as B above,

E = alpha detector efficiency,

F = total calibrated tracer counts for same counting time as sample counts,

W = sample weight (grams or volume in liters),

T = counting time (minutes), and

2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries per gram or liter as follows:

$$LLD = \frac{4.66\sqrt{A_1 T}}{(2.22)(E)(R)(W)(T)}$$

where

A_1 = background count rate,

T = counting time (same for sample and background),

E = alpha detector efficiency,

R = fractional yield ($B-B_1/F$ in calculation),

W = sample weight (grams or volume liters), and

2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.
2. Teflon is a registered trademark of DuPont Co, Wilmington, DE.
3. Hydrogen peroxide stabilizes the +4 plutonium valence necessary for maximum extraction in the TIOA.

References

1. Moore, F.L., "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric acid Solution with Tri (iso-octyl) amine," Analytical Chemistry 30, 908 (1958).
2. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.
3. Johns, F.B., et al., Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0539-17, U.S. E.P.A., Las Vegas, NV, (1979).

PREPARATION OF PLUTONIUM-236 TRACER SOLUTION

Principle

Plutonium-236 has a half-life of 2.85 years and decays to uranium-232. In order to prevent contamination of samples with uranium-232 and its decay products, any stock of plutonium-236 must be periodically decontaminated before use. This should be done every 90 days.

Plutonium-236 is extracted into triisooctylamine (TIOA). The plutonium is stripped from the TIOA with a mixture of HCl and HF and then wet ashed. Aliquots of the cleaned plutonium tracer are coprecipitated with lanthanum fluoride and radioassayed by alpha spectroscopy to determine the specific activity of the tracer solution.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Planchets, stainless steel, 32 mm diameter.
3. Plastic graduated cylinder.
4. Separatory funnels, 1 liter capacity.
5. Suction filter apparatus for 25 mm membrane.
6. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump, and chamber.

Reagents

1. Ethanol, 95 percent reagent.
2. Hydrochloric acid, 12 M. 37 percent reagent.
3. Hydrochloric acid, 9 M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
4. Hydrochloric acid, 3 M/Hydrofluoric acid, 0.1 M mixture. Dilute 250 ml of the 37 percent reagent grade HCl and 3.5 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Store in a plastic bottle.

5. Hydrochloric acid, 1 M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrofluoric acid, 29 M. 48 percent HF reagent.
7. Hydrofluoric acid, 3 M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduated cylinder and storage bottle.
8. Hydrogen peroxide, 50 percent reagent grade.
9. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0799 g $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1 M HCl.
10. Triisooctylamine (TIOA), reagent grade.
11. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml of the triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
12. p-Xylene, reagent grade.

Procedure

1. From the specific activity of the plutonium-236 stock solution, determine the size of the aliquot to be used, that when diluted will result in a final solution of approximately 1 pCi ^{236}Pu/ml.
2. Evaporate the aliquot of ^{236}Pu to dryness in a beaker.
3. Add 10 ml of 12 M HCl and evaporate to dryness.
4. Add 100 ml 9 M HCl to the beaker and warm to 50°C.
5. Add 10 drops of 50 percent hydrogen peroxide to the solution.
6. Equilibrate 100 ml of the 10 percent TIOA solution with 50 ml of warm 9 M HCl by shaking in a separatory funnel for 1 minute.
7. Allow the layers to separate and discard the lower aqueous acid phase.
8. Add the solution from step 5 to the TIOA in the separatory funnel and shake funnel for 2 minutes.
9. Allow phases to separate and discard the lower aqueous acid phase.
10. Wash the TIOA solution with 50 ml 9 M HCl warmed to 50°C. Shake for 1 minute and discard lower aqueous acid phase when separated.

11. Extract the plutonium from the TIOA with 75 ml of 3 M HCl/0.1 M HF mixture warmed to 50°C. Shake funnel for 2 minutes.
12. Drain and save lower aqueous acid phase.
13. Repeat steps 11 and 12. Combine acid strip solution into one clean separatory funnel.
14. Add 100 ml p-xylene to combined strip solution and shake funnel for one minute.
15. Allow phases to separate cleanly; withdraw lower aqueous acid layer into a beaker. Discard p-xylene.
16. Evaporate solution from step 15 to dryness. Do not overheat.
17. Add 10 ml 12 M HCl to residue in beaker and take to dryness. Do not overheat.
18. Take up solution in 250 ml 1 M HCl and filter through a filter membrane using suction. Place filtrate in a storage bottle.
19. Coprecipitate 1 ml aliquots of the stock solution in step 18 by adding each aliquot to 15 ml 1 M HCl in a beaker.
20. Add 1 ml of lanthanum carrier and 5 ml of 3 M HF to each beaker. Mix well and set aside for 30 minutes to precipitate LaF_3 carrying plutonium.
21. Using suction, filter coprecipitated sample through a filter membrane.
22. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
23. Remove clamp and top of funnel with suction on. Allow membrane to dry.
24. Mount membrane carefully on 32 mm planchet using double stick tape.
25. Count sample for 1000 minutes on alpha spectrometer.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.

References

1. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.

RADIOCHEMICAL DETERMINATION OF RADIUM-226 IN SOLID SAMPLES REQUIRING FUSION

Principle

Solid samples are solubilized by fusion with a special flux. The radium-226 in solution is determined by coprecipitation from the sample with barium sulfate. The precipitate is solubilized and sealed in a deemanation tube. After an ingrowth period, the radon-222 is removed into an alpha scintillation counting cell for measurement.

Special Apparatus

1. Metricel DM800 filter membranes or equivalent, 25 mm dia., 0.8 micrometer pore size. See Note 1.
2. Magnetic stirrer and stirring bar.
3. Platinum crucibles, 20 ml with lids.
4. Suction filter apparatus.
5. Tongs for platinum crucibles.

Reagents

1. Acetone-ethanol mixture, 50 percent each reagent by volume.
2. Ammonium sulfate, 10 percent. Dissolve 10 g reagent grade $(NH_4)_2SO_4$ in distilled water and dilute to 100 ml.
3. Barium chloride, 10 mg Ba^{+2}/ml. Dissolve 17.79 g $BaCl_2 \bullet 2H_2O$ in 1 liter distilled water.
4. Barium chloride, 2 mg Ba^{+2}/ml. Dilute 200 ml of the 10 mg/ml barium chloride solution to 1 liter. Filter after 24 hours.
5. Fusion flux. Mix thoroughly 15 mg barium sulfate ($BaSO_4$), 32.9 g potassium carbonate (K_2CO_3), 25.3 g sodium carbonate (Na_2CO_3), 16.8 g sodium tetraborate decahydrate ($Na_2B_4O_7 \bullet 10H_2O$). Heat to expel water, then fuse in a platinum crucible and mix thoroughly by swirling. Cool and grind in a porcelain mortar to pass a 10 to 12 mesh screen. Store in an airtight bottle.

6. Hydrochloric acid, 3M. Dilute 250 ml of the 37 percent HCl reagent to 1 liter with distilled water.
7. Hydrogen peroxide, 3 percent reagent.
8. Hydrofluoric acid, 29M, 48 percent HF reagent.
9. Phosphoric acid, 15M, 85 percent H_3PO_4 reagent.
10. Radium-226 standard solution, 5 to 10 pCi/ml traceable to NBS.
11. Sulfuric acid, 18M, 96 percent H_2SO_4 reagent.
12. Sulfuric acid, 0.1 M. Dilute 6 ml of the 96 percent reagent H_2SO_4 to 1 liter with distilled water.

Procedure

1. Weigh sample using minimum of 0.5 g of soil sample and place in platinum crucible.
2. Add flux and mix, using 8 g of flux for each gram of sample. Do not use less than 4 g of flux (for minimum of 0.5 g soil).
3. Put lid on crucible and place it on tripod over burner. Fuse for 30 minutes.
4. Swirl mixture at least once during fusion.
5. Remove crucible from heat with tongs and swirl mixture until it begins to solidify.
6. Prepare the following solution in a beaker, made up as needed: 120 ml distilled water, 10 ml 18M H_2SO_4, and 5 ml 3 percent H_2O_2.
7. Place platinum crucible and lid in beaker. Fused sample will dissolve away from crucible in about 30 minutes.
8. Remove crucible from solution. Rinse crucible with distilled water and pour back into beaker.
9. Place magnetic stirring bar in beaker and begin stirring.
10. Add 50 ml dilute $BaCl_2$ solution to beaker.
11. Stir contents of beaker for 90 minutes.
12. Remove magnetic stirring bar and wait overnight for the $BaSO_4$ to precipitate.

13. Pour clear liquid off top of beaker so that entire quantity does not have to be filtered.
14. Pour remaining liquid and precipitate into funnel attached to suction filter. Use 0.1 M H_2SO_4 as wash solution and wash filter funnel twice with wash solution.
15. Remove clamp and lift filter funnel carefully to avoid removing filtered precipitate. Use 1/2 filter membrane to wipe precipitate clinging to bottom of filter funnel and place membrane in a platinum crucible.
16. Carefully remove filter membrane from filter frit and place in platinum crucible.
17. Add 25 drops 29M HF and 0.3 ml 10 percent $(NH_4)_2SO_4$ solution to the crucible.
18. Place crucible on hotplate at low temperature and evaporate contents to dryness.
19. Add 2 ml of acetone-alcohol mixture and burn off solvents with a match.
20. Put top on crucible, place on tripod over burner, and heat until ashed (about 10-15 minutes).
21. Remove from heat and add 1 ml 15M H_3PO_4.
22. Place crucible on hot place at low setting for 15 minutes. Turn up to higher temperature for additional 30 minutes.
23. Hold crucible with platinum-tip tongs in the hottest part of flame of a burner.
24. When white material dissolves and the bubbling and fumes decrease, swirl crucible in upper part of flame for one minute. The result is a clear material which solidifies when removed from the heat.
25. Place crucible in hot water bath.
26. Fill crucible with 3M HCl.
27. Leaving lid off, allow liquid in crucible to evaporate slowly (2 1/2 - 3 hours) until almost completely evaporated with white crystals remaining.

28. Fill crucible approximately 1/2 full with deionized water and allow the crystals to dissolve.
29. Carefully pour solution from crucible into deemanation storage tube described in Deemanation Procedure. Rinse crucible with deionized water.
30. Flame seal tube for storage as described in Deemanation Procedure.

Notes

1. Metricel is a trademark of Gelman Sciences Inc., Ann Arbor, MI.

References

1. Standard Methods for the Examination of Water and Waste Water, 15th Ed., American Public Health Association, Washington, D.C. (1980).

RADIOCHEMICAL DETERMINATION OF RADIUM-226 IN URINE

Principle

Barium-133 is added as a tracer to urine sample. Alkaline earth cations are precipitated from the urine with sodium carbonate. The precipitate containing barium and radium is further treated with nitric acid to remove organic material. The sample is solubilized and stored in a deemanation tube for three weeks. Radium-226 is determined by the De-emanation Procedure for radium-226.

Special Apparatus

1. Centrifuge.
2. Gamma ray analyzer with NaI(Tl) well crystal.
3. Glassware.

Reagents

1. Barium-133 tracer. Approximately 5 nCi/ml.
2. Nitric acid 16M, 70 percent HNO_3 reagent.
3. Nitric acid 3M. Dilute 187 ml of the reagent grade HNO_3 to 1 liter with distilled water.
4. Sodium carbonate, 1.5M. Dissolve 159g Na_2CO_3 in 900 ml distilled water and dilute to 1 liter.

Procedure

1. Add 1 ml barium-133 tracer to 250 ml urine at room temperature.
2. Add 25 ml 1.5M Na_2CO_3 and stir with a magnetic stirrer for 30 minutes.
3. Digest at 50° C for 30 minutes and cool in an ice bath.
4. Centrifuge and discard supernate. Dissolve precipitate in 10 ml 16M HNO_3.
5. Evaporate to dryness and take up in 25 ml of 3M HNO_3.

6. Pipette 1 ml of the sample solution into a tube for gamma ray counting. Compare with 1 ml barium-133 tracer to obtain chemical yield.
7. Transfer the whole sample to a radon emanation tube. Seal and store for three weeks.
8. Proceed with de-emanation procedure for radium-226.

References

1. Standard Methods for the Examination of Water and Waste Water, 15th Ed., American Public Health Association, Washington, D.C. (1980).

RADIOCHEMICAL DETERMINATION OF RADIUM-226 IN WATER SAMPLES

Principle

Radium-226 in solution is determined by coprecipitation from the sample with barium sulfate. The sample is then analyzed using the de-emanation procedure.

Special Apparatus

1. Metricel DM-800 filter membrane, 25-mm dia., 0.8-micrometer pore size or equivalent. See Note 1.
2. Pleated filter paper.
3. Platinum crucibles, 20 to 30 ml and lids.
4. Crucible tongs for platinum.
5. Glassware.

Special Reagents

1. Acetone-ethanol, 50 percent each by volume.
2. Ammonium sulfate, 10 percent. Dissolve 10 g $(NH_4)_2SO_4$ in distilled water and dilute to 100 ml with distilled water.
3. Barium chloride stock solution, 10 mg Ba^{+2}/ml. Dissolve 17.79 g $BaCl_2 \bullet 2H_2O$ in 1 liter of distilled water.
4. Barium chloride dilute solution, 2 mg Ba^{+2}/ml. Dilute 200 ml of the barium chloride stock solution to 1 liter in a volumetric flask with distilled water.
5. Hydrochloric acid, 12$\underline{M}$: 37 percent HCl reagent.
6. Hydrochloric acid, 3$\underline{M}$. Dilute 250 ml of the reagent grade HCl to 1 liter with distilled water.
7. Hydrofluoric acid, 29$\underline{M}$: 48 percent HF reagent.
8. Phosphoric acid, 15$\underline{M}$: 85 percent H_3PO_4 reagent.
9. Radium-226 standard solution, approximately 5 to 10 pCi/ml, traceable to the National Bureau of Standards.
10. Sulfuric acid, 18$\underline{M}$: 96 percent H_2SO_4 reagent.

11. Sulfuric acid, 0.05M. Dilute 1.6 ml of the H_2SO_4 reagent to 1 liter with distilled water.

Procedure

1. If water sample is not clear, filter a one liter aliquot through a pleated filter paper. Save any precipitate if the radium content of the precipitate is needed. It is then analyzed using the procedure for solid samples.
2. Place the water sample in a 1.5 liter beaker, add a magnetic stirring bar and place on a stirrer.
3. Add the following to the water sample with stirring: 20 ml 12M HCl, 50 ml dilute $BaCl_2$ reagent, and 20 ml 18M H_2SO_4.
4. Cover sample and allow to stir for a minimum of 30 minutes to precipitate $BaSO_4$.
5. Remove magnetic stirring bar and allow mixture to stand overnight.
6. Decant clear liquid off the top so that entire quantity does not have to be filtered.
7. Decant remaining liquid and precipitate into funnel attached to suction filter. Use 0.05M H_2SO_4 as wash solution and wash filter funnel twice with wash solution.
8. Remove clamp and lift filter funnel carefully to avoid removing filtered precipitate. Use half of a filter membrane to wipe precipitate clinging to bottom of filter funnel and place membrane in a platinum crucible.
9. Carefully remove filter membrane from the filter apparatus and place in platinum crucible.
10. Add 25 drops 29M HF and 0.3 ml 10 percent $(NH_4)_2SO_4$ solution to volatilize silica as SiF_4.
11. Place crucible on hotplate at low temperature and take to dryness.
12. Add 2 ml of acetone-alcohol mixture and burn off solvents with a match.

13. Put top on crucible, place on tripod over burner, and heat until ashed (about 10-15 minutes).
14. Remove from heat and add 1 ml 15M H_3PO_4.
15. Place crucible on hot plate at low setting for 15 minutes. Turn up to higher temperature for additional 30 minutes.
16. Hold crucible with platinum-tip tongs in the hottest part of flame of a burner.
17. When white material dissolves and the bubbling and fumes decrease, swirl crucible in upper part of flame for one minute. The result is a clear material which solidifies when removed from the heat.
18. Place crucible in hot water bath.
19. Fill the crucible almost full with 3M HCl.
20. Leaving lid off, allow liquid in crucible to evaporate slowly (1 1/2 - 3 hours) until almost completely evaporated with white crystals remaining.
21. Fill crucible approximately half full with deionized water and allow the crystals to dissolve.
22. Carefully pour solution from crucible into de-emanation storage tube described in De-emanation Procedure. Rinse crucible with distilled water.
23. Flame seal tube for storage as described in the Radium-226 De-emanation Procedure and proceed.

Notes

1. Metricel is a trademark of Gelman Sciences, Inc., Ann Arbor, MI.

References

1. Standard Methods for the Examination of Water and Waste Water, 15th Ed., American Public Health Association, Washington, D.C. (1980).

RADIOCHEMICAL DETERMINATION OF RADIUM-226

De-emanation Procedure

Principle

After sample preparation is completed, individual samples are sealed in disposable storage tubes. Radon-222 ingrowth proceeds through three weeks storage of the tubes. The tubes are then connected to a gas manifold and the accumulated radon-222 is swept into evacuated Lucas alpha scintillation counting cells. The alpha activity in the cells is measured after five hours ingrowth of radon-222 progeny.

Special Apparatus

1. De-emanation manifold assembly.
2. Lucas alpha scintillation cells.
3. Photomultiplier tube assembly and associated electronics.
4. Tank of nitrogen.
5. Glass-sealing torch.
6. Vacuum pump assembly.
7. Pyrex brand glass tubing, 15-mm inside diameter, 60-cm lengths.
8. Acid dichromate cleaning solution.
9. Vinyl tubing, 1.3 cm inside diameter, 1.6 cm outside diameter.

Procedure

1. Clean 60-cm lengths of glass tubing in dichromate cleaning solution and dry.
2. Flame seal one end of the individual sections of the glass tubing.
3. Starting approximately 10 cm from the open end of a section of the tubing, soften the tubing in a flame and form a constriction approximately 6.5 cm long and 0.6 cm diameter.
4. Transfer prepared sample to de-emanation tube using distilled water as wash. Fill to within 1.3 cm of constriction.

5. Flame seal tube at constriction without overheating.
6. Store sample-containing sealed tubes for at least 21 days.
7. Soak one end of each of two 9 cm long by 1.25 cm in diameter pieces of vinyl tubing in acetone until slight swelling occurs.
8. Place a serum stopper in the solvent treated end of each piece of tubing so that the tubing surrounds the sleeve of the stopper.
9. Insert 26-gauge hypodermic needles in the rubber serum stoppers.
10. Soak the other ends of the vinyl tubing in acetone until swelling is evident.
11. Slip the solvent-treated tubing over the sealed end of the sample tube. Leave the needle inserted in the stopper to relieve pressure as tubing dries.
12. Remove needles from stoppers after 24 hours.
13. Evacuate Lucas scintillation cells by inserting needle connected to vacuum line through stopper attached to neck of cell.
14. Disconnect cell from vacuum line with vacuum pump operating.
15. Set up radon transfer manifold as shown in the cell evacuation illustration (Figure 1).
16. Insert needle from vacuum line into lower stopper of the vacuum tube. Insert needle attached to vacuum gauge into the same stopper.
17. Remove vacuum line needle and check gauge for possible leak.
18. Reapply vacuum to tube and close upper valve.
19. Insert needle from vacuum line into upper stopper of the sample tube being careful not to break tip of tube with needle.
20. Repeat step 19 for other end of sample tube.
21. Allow 10 minutes to elapse in order to check for air leaks at both ends of sample tube. A leak is indicated by partial refilling of the collapsed vinyl tubing.
22. Attach sample cell to manifold as shown in purging illustration (Figure 2).
23. Break both top and bottom tips of sample tube using long nose pliers.

24. Record time.
25. Put rubber sealant on the vinyl tubing in the area of the broken glass tips as a precaution against puncture of the tubing.
26. Cautiously open top valve to permit pressure equalization between sample tube and Lucas cell, being careful not to draw up sample liquid into drying tube.
27. Close upper valve.
28. Start nitrogen purge with flow rate barely detectable through hole in tubing.
29. Flush valve, and, with valve closed, insert needle from flow tube into lower stopper of sample tube.
30. Cautiously open lower valve to control flow of nitrogen into sample tube. The bubble rate should be between 15 and 45 per minute.
31. For a period of 30 minutes open upper valve briefly in order to equalize pressure between Lucas cell and sample tube.
32. After 30 minutes, open upper valve completely and open lower valve to increase bubble rate.
33. When nitrogen flow has stopped and vinyl tubing has expanded to shape, simultaneously remove needles from stoppers of Lucas cell and lower stopper of sample tube.
34. The Lucas cell is stored for 5 hours prior to counting for ingrowth of radon-222 progeny.
35. Count the sample for 1000 minutes.
36. Dispose of needles and drying tube.
37. Clean upper valve by the following steps: (a) disassemble valve, (b) submerge in acetone and rinse with water, (c) submerge in mineral spirits, (d) wash in hot soapy water and rinse, and (e) dry in oven at 75° C.

Calculations

Calculate the concentration, Z, of radium-226 in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(E)(V)} \times \frac{1}{1-e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{\lambda t_3}{1-e^{-\lambda t_3}}$$

where

λ = decay constant for radon-222 (t 1/2 = 3.825 days),
t_1 = time interval allowed for ingrowth or radon from radium,
t_2 = time interval between de-emanation and counting,
t_3 = counting time,
C_1 = observed count rate of sample,
C_B = background count rate,
E = calibration constant of the scintillation cell in counts per unit time per picocurie of radon plus decay products (All of the corrections can be obtained directly or indirectly from Table 1),
V = sample volume (liters), and
2.22 = dpm/pCi.

Sample Calculation

Assume the following data:

t_1 = 13d., 14 h., 6 m,
t_2 = 4 h., 15 m,
t_3 = 16 h., 30 m,
C_1 = 199.2 counts/hour,
C_B = 9.3 counts/hour, and
E = 151.1 counts/hour/dpm. See Note 1.

From Table 1,

$1\text{-}e^{-\lambda t_1} = 1. - 0.09484 \times 0.89969 \times 0.99925 = 0.91474,$

$e^{-\lambda t_2} = 0.97025 \times 0.99811 = 096842,$ and

$\lambda t_3 / (1\text{-}e^{-\lambda t_3}) = 1.06358$ (by linear interpolation).

From these data,

$$\text{pCi Ra} = \frac{(199.2 - 9.3)}{(151.1)\ (2.22)} \times \frac{1}{0.91474} \times \frac{1}{0.96842} \times 1.06358 = 0.680.$$

Calculate the lower limit of detection (LLD) in picocuries per liter as follows:

$$\text{LLD} = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(V)(T)}$$

where

C_B = background count rate,
T = counting time, and
E = calibration constant of the scintillation cell in counts per unit time per picocurie of radon plus decay products in counts per hour per dpm.

This LLD is valid if the background counting time is approximately equal to the sample counting time.

Notes

1. The calibration constant is determined by sealing a known quantity of radium-226 in a de-emanation tube. After 21 days storage, the radon

is transferred to a Lucas cell and counted. The Lucas cells are individually calibrated. The radium-226 used is traceable to the National Bureau of Standards. Approximately 5-10 of radium-226, accurately known, is used for each calibration.

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TABLE 1

A. Decay of Radon (in minutes, hours, and days)
B. Growth of Radon from Radium (in days).
C. Multiplicative Factor for Correction of Radon Activity for Decay during Counting (in hours)

(Based on 3.825 days as half-life of radon)

Time	A. $e^{-\lambda t}$			B. $1-e^{-\lambda t}$	C. $\frac{\lambda t}{1-e^{\lambda t}}$
	Minutes	Hours	Days	Days	Hours
0	1.000,00	1.000,00	1.000,00	0.000,00	1.000,00
1	0.999,87	0.992,48	0.834,27	0.165,73	1.003,72
2	0.999,75	0.985,01	0.696,00	0.304,00	1.007,54
3	0.999,62	0.977,60	0.580,65	0.419,35	1.011,39
4	0.999,59	0.970,25	0.484,42	0.515,58	1.015,16
5	0.999,37	0.962,95	0.404,14	0.595,86	1.018,98
6	0.999,25	0.955,71	0.337,16	0.662,84	1.022,83
7	0.999,12	0.948,52	0.281,28	0.718,72	1.026,65
8	0.998,99	0.941,39	0.234,66	0.765,34	1.030,51
9	0.998,87	0.934,31	0.195,77	0.804,23	1.034,36
10	0.998,74	0.927,27	0.163,33	0.836,67	1.038,23
11	0.998,62	0.920,31	0.136,26	0.863,74	1.042,10
12	0.998,49	0.913,38	0.113,68	0.886,32	1.045,97
13	0.998,37	0.906,51	0.094,84	0.905,16	1.049,88
14	0.998,24	0.899,69	0.079,12	0.920,88	1.053,79
15	0.998,11	0.892,93	0.066,01	0.933,99	1.057,69
16	0.997,99	0.886,21	0.055,07	0.944,93	1.061,61
17	0.997,86	0.879,55	0.045,94	0.954,06	1.065,54
18	0.997,74	0.872,93	0.038,33	0.961,67	1.069,49
19	0.997,61	0.866,36	0.031,98	0.968,02	1.073,44
20	0.997,49	0.859,85	0.026,68	0.973,32	1.077,40
21	0.997,36	0.853,38	0.022,25	0.977,75	1.081,37
22	0.997,24	0.846,96	0.018,57	0.981,43	1.085,35
23	0.997,11	0.840,59	0.015,49	0.984,51	1.089,34
24	0.996,99	0.834,27	0.012,92	0.987,08	1.093,33
25	0.996,86	0.827,99	0.010,78	0.989,22	1.097,34

TABLE 1 (Continued)

Time	A. $e^{-\lambda t}$			B. $1-e^{-\lambda t}$	C. $\frac{\lambda t}{1-e^{\lambda t}}$
	Minutes	Hours	Days	Days	Hours
26	0.996,73	0.821,77	0.008,99	0.991,01	1.101,36
27	0.996,61	0.815,58	0.007,50	0.992,50	1.105,39
28	0.996,48	0.809,45	0.006,26	0.993,74	1.109,45
29	0.996,36	0.803,36	0.005,22	0.994,78	1.113,47
30	0.996,23	0.797,32	0.004,36	0.995,64	1.117,52
31	0.996,11	0.791,32	0.003,63	0.996,37	1.121,58
32	0.995,98	0.785,37	0.003,03	0.996,97	1.125,66
33	0.995,86	0.779,46	0.002,53	0.997,47	1.129,74
34	0.995,73	0.773,60	0.002,11	0.997,89	1.133,83
35	0.995,61	0.767,78	0.001,76	0.998,24	1.137,94
36	0.995,48	0.762,01	0.001,47	0.998,53	1.142,05
37	0.995,36	0.756,28	0.001,23	0.998,77	1.146,17
38	0.995,23	0.750,59	0.001,02	0.998,98	1.150,30
39	0.995,11	0.744,94	0.000,85	0.999,15	1.154,44
40	0.994,98	0.739,34	0.000,71	0.999,29	1.158,59
41	0.994,85	0.733,78	0.000,59	0.999,41	1.162,75
42	0.994,73	0.728,26	0.000,50	0.999,50	1.166,92
43	0.994,60	0.722,78	0.000,41	0.999,59	1.171,09
44	0.994,48	0.717,34	0.000,34	0.999,66	1.175,28
45	0.994,35	0.711,95	0.000,29	0.999,71	1.179,47
46	0.994,23	0.706,59	0.000,24	0.999,76	1.183,68
47	0.994,10	0.701,23	0.000,20	0.999,80	1.187,89
48	0.993,98	0.696,00	0.000,17	0.999,83	1.192,12
49	0.993,85	0.690,77	0.000,14	0.999,86	1.196,35
50	0.993,73	0.685,57	0.000,12	0.999,88	1.200,60
51	0.993,60	0.680,42	0.000,10	0.999,90	1.204,85
52	0.993,48	0.675,30	0.000,08	0.999,92	1.209,11
53	0.993,35	0.670,22	0.000,07	0.999,93	1.213,38
54	0.993,23	0.665,18	0.000,06	0.999,94	1.217,66
55	0.993,10	0.660,18	0.000,05	0.999,95	1.221,95
56	0.992,98	0.655,21	0.000,04	0.999,96	1.226,25
57	0.992,85	0.650,28	0.000,03	0.999,97	1.230,56
58	0.992,73	0.645,39	0.000,03	0.999,97	1.234,88
59	0.992,60	0.640,54	0.000,02	0.999,98	1.239,21
60	0.992,48	0.635,72	0.000,02	0.999,98	1.243.54

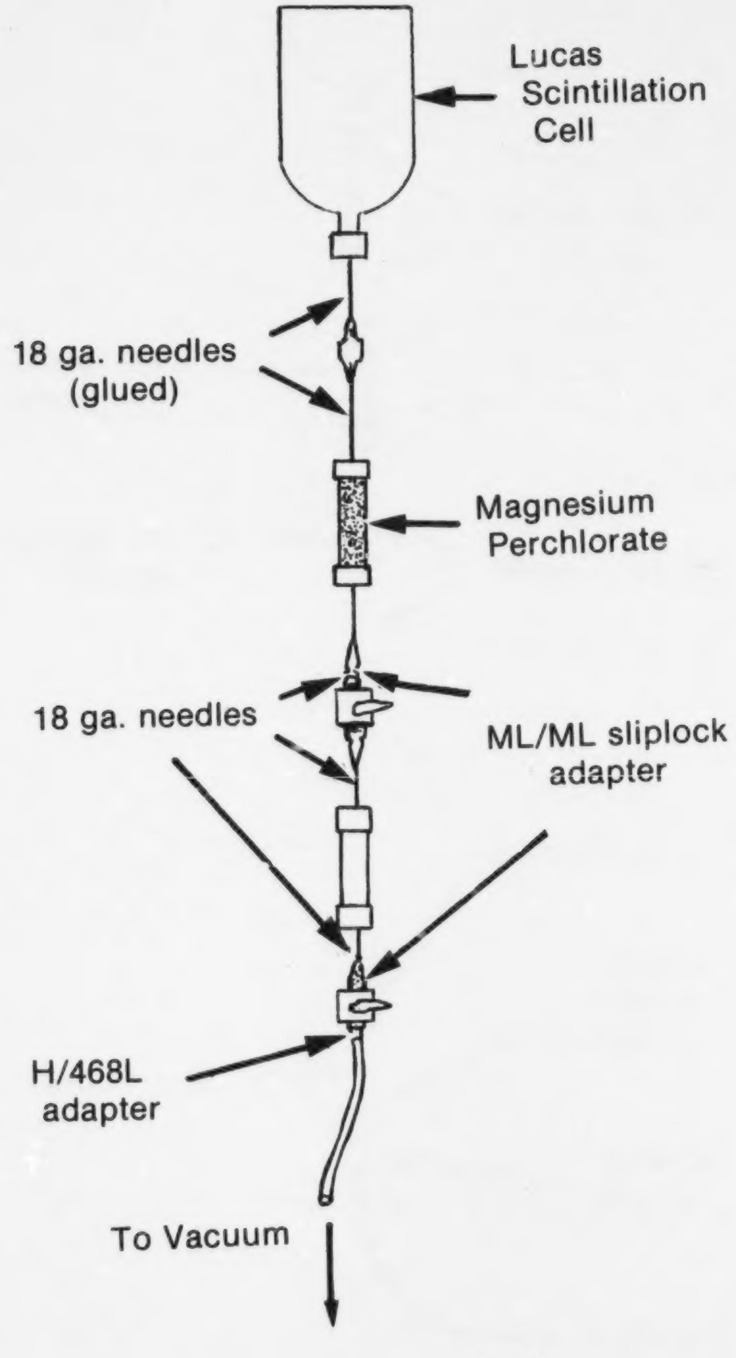
Lucas
Scintillation
Cell
18 ga. needles
(glued)
Magnesium
Perchlorate
18 ga. needles
ML/ML sliplock
adapter
H/468L
adapter
To Vacuum

Figure 1. Cell evacuation assembly.

Ra-04-9

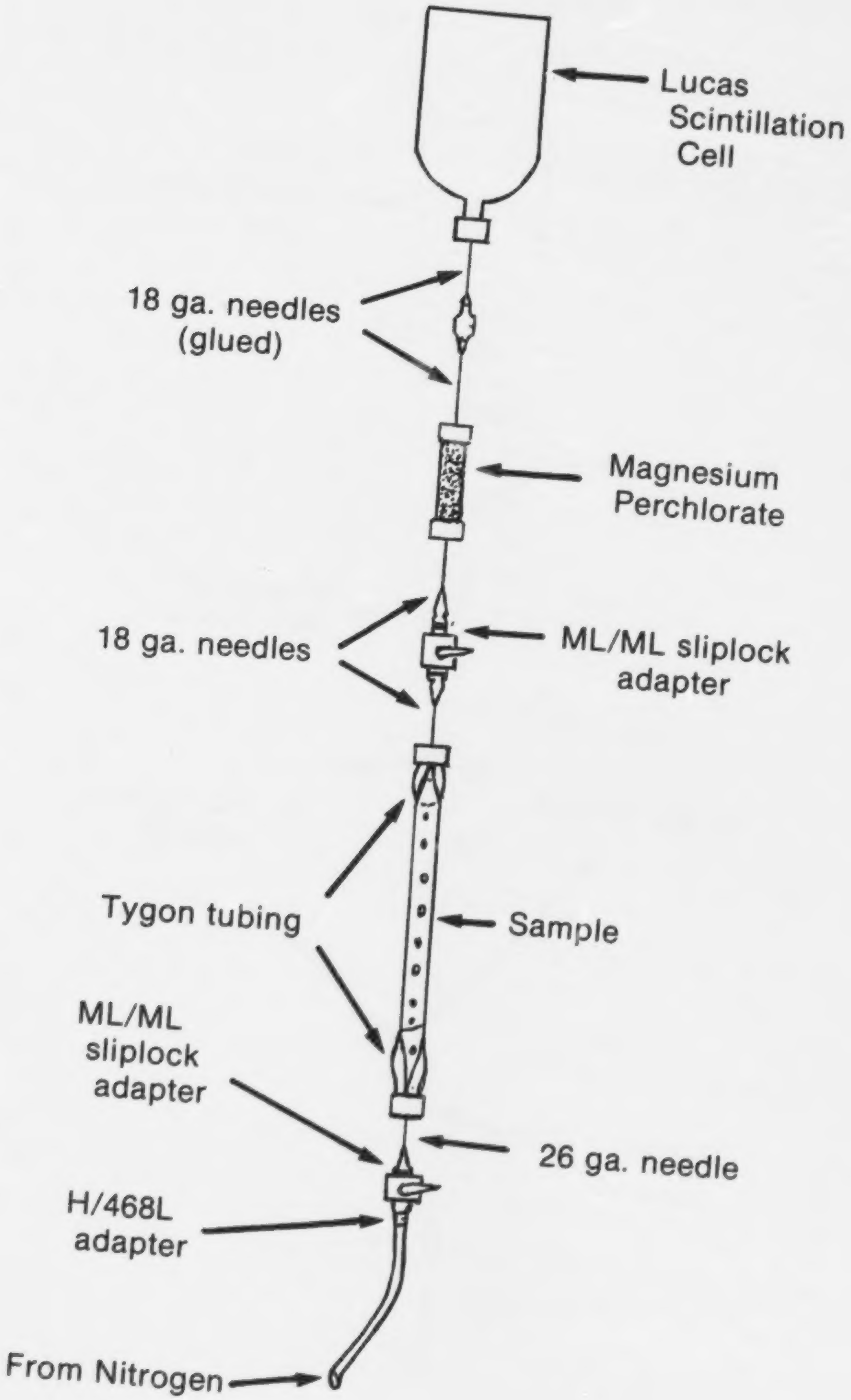
Lucas
Scintillation
Cell
18 ga. needles
(glued)
Magnesium
Perchlorate
18 ga. needles
ML/ML sliplock
adapter
Tygon tubing
Sample
ML/ML
sliplock
adapter
26 ga. needle
H/468L
adapter
From Nitrogen

Figure 2. **Cell purging assembly.**

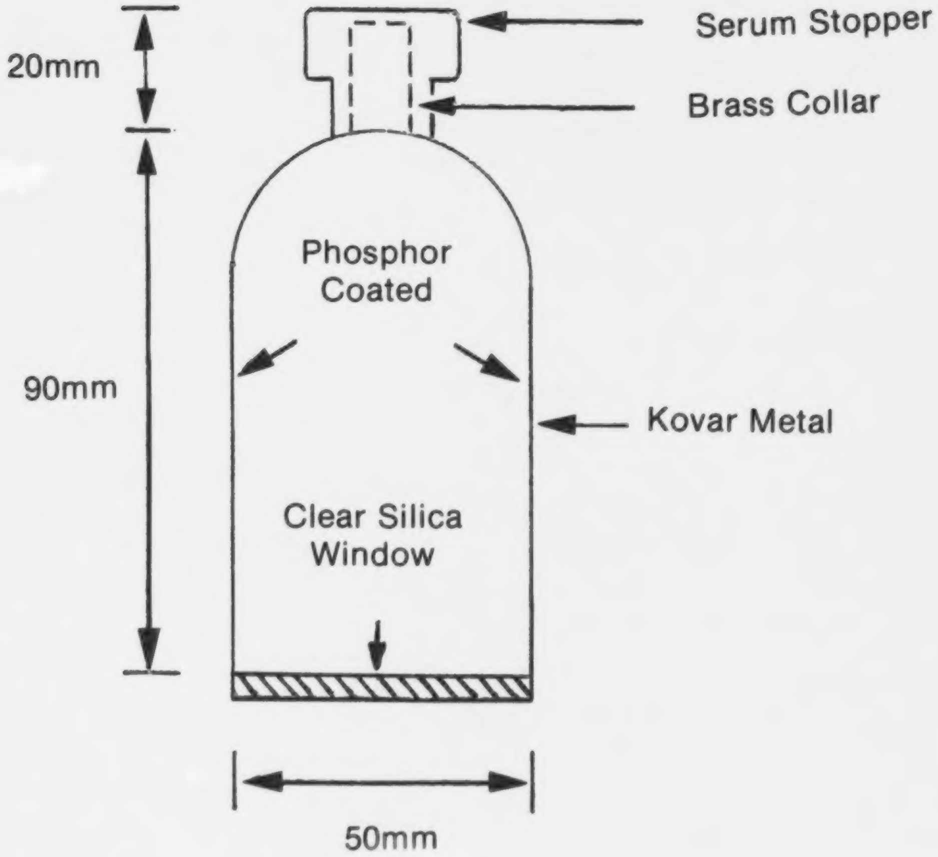
20mm
Serum Stopper
Brass Collar
Phosphor Coated
90mm
Kovar Metal
Clear Silica Window
50mm

Figure 3. **Lucas type scintillation cell.**

RADIOCHEMICAL DETERMINATION OF RADIUM-228 IN WATER SAMPLES

Principle

The radium solution from the radium-226 determination is saved and the radium is reprecipitated as a radium-barium sulfate. This precipitate is dissolved in a pentasodium diethylenetriamine pentaacetate solution. The radium-228 is a weak beta emitter and decays to actinium-228, which is allowed to ingrow for three days. The actinium-228 is then extracted with Di-2-ethylhexylphosphoric acid and back-extracted with nitric acid. The actinium-228 is beta counted in a low background proportional counter.

Special Apparatus

1. Centrifuge.
2. Planchets, stainless steel, 5 cm diameter.
3. Separatory funnels, 125 ml, 2 liter capacity.
4. Magnetic stirrer and stirring bars.
5. Glassware.
6. Suction filter apparatus.

Reagents

1. Acetic acid, glacial 17.4$\underline{M}$. $HC_2H_3O_2$ reagent.
2. Acetic acid 6$\underline{M}$. Dilute 345 ml of the reagent grade $HC_2H_3O_2$ to one liter with distilled water.
3. Actinium wash solution. Dissolve 100 g monochloroacetic acid and 2.4 ml of 41 percent Na_5DTPA in 800 ml of distilled water and dilute to 1 liter. Adjust the pH to 3.0 with NaOH pellets (approximately 25.4 g NaOH).
4. Ammonium hydroxide 15$\underline{M}$. Reagent grade NH_4OH.
5. Barium carrier, 10 mg Ba^{+2}/ml. Dissolve 17.78 g $BaCl_2 \bullet 2H_2O$ in 800 ml distilled water and dilute to 1 liter. Allow to stand 24 hours and filter.
6. Barium carrier, 5 mg Ba^{+2}/ml. Dissolve 4.45 g $BaCl_2 \bullet 2H_2O$

in 400 ml distilled water and dilute to 500 ml.

7. Bismuth carrier, 20 mg Bi^{+3}/ml. Dissolve 46.4 g $Bi(NO_3)_3 \bullet 5H_2O$ in 800 ml distilled water and dilute to 1 liter.
8. Chloroacetic acid, 2M. Add 189 g of reagent grade chloroacetic acid to a beaker, dissolve in distilled water and dilute to 1 liter.
9. Diammmonium citrate, 2M. Dissolve 226.2 g dibasic ammonium citrate, $(NH_4)_2HC_6H_5O_7$, in distilled water and dilute to 500 ml.
10. Di-2-ethylhexylphosphoric acid, HDEHP, 15 percent in n-heptane. Dilute 150 ml HDEHP to 1 liter with n-heptane and transfer to a 2-liter separatory funnel. Wash the HDEHP twice with 200 ml aliquots of a 1:1 mixture of 2M diammonium citrate and 15M NH_4OH. The mixture is prepared by adding 100 ml 15M NH_4OH to 100 ml 2M diammonium citrate in a beaker and mixing. Add to the separatory funnel containing the HDEHP. Shake for one minute, releasing pressure frequently. Allow the layers to separate and discard lower layer. Wash the HDEHP twice with 4M HNO_3, discarding the lower layer each time after shaking for one minute. Store the cleaned HDEHP in a polyethylene bottle. Immediately before using the HDEHP solution, the amount to be used is washed first with an equal volume of distilled water and then with one-half the volume of actinium wash. The lower layers are discarded each time after shaking for one minute.
11. Diethylenetriamine pentaacetic acid, pentasodium salt, Na_5 DTPA, 41 percent reagent solution.
12. Diethylenetriamine pentaacetic acid, pentasodium salt, Na_5DTPA, 0.17M, pH 10. Add 209 ml of the 41 percent Na_5 DTPA solution to 400 ml of distilled water and filter through glass wool with suction. Dilute to 1 liter with distilled water and adjust to pH 10 using either perchloric acid or sodium hydroxide (usually requires 10 to 12 ml perchloric acid). Store in a polyethylene bottle.

13. n-Heptane. Reagent grade.
14. Hydrochloric acid, 12M, 37 percent HCl reagent.
15. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
16. Lead carrier, 100 mg Pb^{+2}/ml. Dissolve 160 g reagent grade $Pb(NO_3)_2$ in 800 ml distilled water and dilute to 1 liter.
17. Nitric acid, 16M, 70 percent HNO_3 reagent.
18. Nitric acid, 4M. Dilute 250 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
19. Nitric acid, 1M. Dilute 63 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
20. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
21. Sodium hydroxide. Reagent grade pellets.
22. Sodium sulfate, 20 percent. Dissolve 20 g anhydrous Na_2SO_4 in 80 ml distilled water and dilute to 100 ml.
23. Sulfuric acid, 18M, 96 percent H_2SO_4 reagent.
24. Sulfuric acid, 4M. Dilute 222 ml of the 96 percent reagent grade H_2SO_4 to 1 liter with distilled water.

Procedure

1. Transfer 1,000 ml of the water to a 1,500 ml beaker. Adjust the pH to approximately 1.0 with 16M HNO_3 and add 200 mg of lead carrier.
2. Add 100 ml 18M H_2SO_4 and heat to 70°C with stirring for one hour. Allow the lead sulfate to settle overnight.
3. Carefully decant as much clear liquid as possible without losing any precipitate. Pour equal volumes of the remaining liquid into two centrifuge tubes of equal volume (40-ml or 100-ml). Centrifuge and decant supernate. If necessary, repeat until all precipitate has been collected in the two centrifuge tubes. Slurry the precipitate in one tube with 4M H_2SO_4 and transfer quantitatively to the other tube using 4M H_2SO_4 as wash.

Centrifuge and discard the supernate.

4. Place a stirring bar in the tube containing the $PbSO_4$, add 1 ml of glacial acetic acid, 6 ml of 41 percent DTPA, and 1 ml distilled water. Heat with stirring until dissolution is complete.
5. Add with stirring, 20 mg bismuth carrier and 2 ml 18M H_2SO_4. Digest 5 to 10 minutes in a hot water bath, cool, centrifuge, and discard supernate. See Note 1.
6. Add 15 ml of 0.17M DTPA to the precipitate, place in a boiling water bath and heat with stirring to dissolve the precipitate (dissolution may require 20 minutes).
7. When the precipitate has dissolved in step 6, add 1 ml of barium carrier (10 mg/ml), 1 ml Na_2SO_4 (20 percent), dilute to 28 ml with distilled water, and then add 2 ml of 6M acetic acid. Heat in a hot water bath for five minutes while stirring with a magnetic stirring bar.
8. Transfer to an ice bath. Allow to cool for five minutes with stirring. Remove stirring bar and centrifuge. Decant and discard supernate.
9. Repeat steps 6, 7, and 8 omitting the addition of Ba^{+2} in step 7. Record the time the acetic acid is added. See Note 2.
10. To the $BaSO_4$ precipitate, add 15 ml 0.17M DTPA, heat and stir until all dissolves.
11. Allow solution to cool, stopper centrifuge tube and store for at least 36 hours to allow for Ac-228 ingrowth.
12. After the ingrowth period, place sample in a boiling water bath, insert a magnetic stirring bar and stir until any precipitate that may have formed during the ingrowth period has dissolved. Then add 1 ml 20 percent Na_2SO_4, dilute to 28 ml with distilled water and add 2 ml of 6M acetic acid. Record time. See Note 3.

13. Allow mixture to heat in the boiling water bath for five minutes with stirring, then remove stirring bar and place centrifuge tube in an ice bath for five minutes. Centrifuge and decant supernate into a clean 40-ml centrifuge tube. Rinse walls with 2 to 3 ml of water, exercising care not to disturb precipitate. Add wash to the tube containing the supernate.
14. Add 1 ml of barium carrier (5mg/ml) to the centrifuge tube containing the supernate. Heat with stirring in a boiling water bath for five minutes. Cool in a ice water bath for five minutes and centrifuge. See Note 4.
15. Quantitatively transfer supernate to a 100-ml beaker containing 5 ml of 2M monochloracetic acid. Measure the pH to confirm that it is 3.0. See Note 5.
16. Transfer the solution to a 125-ml separatory funnel. Add 100 ml of cleaned and actinium washed 15 percent HDEHP using a portion to wash the 100-ml beaker. See Note 6.
17. Shake vigorously for two minutes (relieve pressure as needed). Allow layers to separate and discard lower (aqueous) phase.
18. Add 10 ml of the actinium wash solution. Shake for one minute, allow layers to separate and discard lower (aqueous) layer.
19. Repeat step 18.
20. Add 10 ml of 1M HNO_3. Shake for one minute, allow layers to separate, and collect lower layer in an 80-ml beaker.
21. Repeat step 20 using 5 ml of 1M HNO_3. Combine lower aqueous layer in 80-ml beaker containing aqueous fraction from step 20. Discard organic phase.
22. Evaporate solution to dryness on a 5 cm planchet. Continue heating planchet until all nitric acid vapors have been removed.
23. Count sample and compute Ra-228 concentration. See Note 7.

Calculations

Calculate the concentration, Z, of radium-228 in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(Y)(E)(V)\ (1-e^{-0.113t_1})\ (e^{-0.113t_2})}$$

where

C_1 = sample count rate,

C_B = background count rate,

Y = chemical yield based on counting rate of spike added and recovered (see Note 7),

E = beta counting efficiency,

V = sample size (liters),

t_1 = actinium-228 period of ingrowth from radium-228 (hours) (see steps 9 and 12),

t_2 = actinium-228 decay period (hours) measured from the actinium separation (step 12) to the mid-time of the beta count, and

2.22 = dpm/pCi.

Calculate the lower limit of detection (LLD) in picocuries per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(Y)(E)(V)(T)}$$

where

Y = chemical yield,

E = beta counting efficiency,

V = sample volume (liters), and

T = counting time.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

Notes

1. If Ra-226 is determined by de-emanation of Rn-222 between steps 4 and 5, the supernate will contain the Bi-210 that grew in during the 30-day Rn-222 ingrowth period and can be used to determine Pb-210 (For a 30-day ingrowth period, Bi-210 will be 98.4 percent of its equilibrium value).
2. Steps 6, 7, and 8 are performed to remove all Ac-228 present. The second $BaSO_4$ precipitation with acetic acid provides an actinium free precipitate and begins the measured ingrowth of the Ac-228 from the Ra-228 present.
3. The precipitation of $BaSO_4$ in step 10 isolates the actinium in the supernate and ends the Ac-228 ingrowth period.
4. The second $BaSO_4$ precipitation insures complete removal of the radium.
5. It is important that the pH of the solution containing the actinium is 3.0. If necessary, adjust pH with additional $2\underline{M}$ monochloracetic acid.
6. It is important that the HDEHP be washed with an equal volume of distilled water and half volume aliquot of actinium wash solution immediately prior to using.
7. There is no isotope of actinium available to monitor the chemical yield of Ac-228. To determine the chemical yield, a second 1-liter sample of acidified water is spiked with a known quantity of Ra-228 and analyzed in the exact manner and at the same time as the unknown sample. The chemical yield determined for the spiked sample is assumed equal to that for the unknown sample. The spiked sample should be analyzed with each batch of unknown samples.

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RADIOCHEMICAL DETERMINATION OF RADIOSTRONTIUM IN FOOD ASH AND OTHER SOLID SAMPLES

Principle

Barium, calcium and strontium carriers are added to the ashed sample. Magnesium is precipitated and removed from the sample at pH 3.8. Barium and strontium are adsorbed on a cation exchange resin allowing calcium to pass through. The barium and strontium are selectively eluted and the strontium is precipitated. Strontium-89 and strontium-90 are radioassayed separately by measuring the ingrowth of yttrium-90.

Special Apparatus

1. Graduated separatory funnel as reservoir for column, 1 liter capacity.
2. Ion exchange column, 2.5 cm internal diameter, 18 cm in length.
3. Metricel DM800 membrane filters or equivalent, 25 mm diameter, 0.8 micrometer pore size. See Note 1.
4. Nickel crucible, 250 ml volume and lid.
5. Stainless steel planchets, 5 cm diameter.
6. Suction filter apparatus.
7. Centrifuge, floor model.
8. Glassware.
9. Blast burner.
10. pH meter.
11. Magnetic stirrer.

Reagents

1. Ammonium hydroxide, 15M. Reagent grade NH_4OH.
2. Ammonium hydroxide, 6M. Dilute 405 ml NH_4OH reagent to 1 liter with distilled water.
3. Barium carrier, 5.0 mg Ba^{+2}/ml. Dissolve 9.5 g $Ba(NO_3)_2$ in 900 ml of distilled water. Add 1 ml of 16M HNO_3 and dilute to

1 liter with distilled water.

4. Calcium nitrate, 2M. Dissolve 472 g $Ca(NO_3)_2 \bullet 4H_2O$ in 750 ml distilled water. Dilute to 1 liter with distilled water.
5. Cation exchange resin, Dowex 50WX8, 50-100 mesh, Na^+ form, or equivalent. Wash 40 ml resin (H^+) with 600 ml 4M NaCl. Wash all excess NaCl from resin with water and check for chloride with 0.1M $AgNO_3$ before using resin.
6. Ethanol, 95 percent reagent.
7. Ethylenediamine tetraacetic acid disodium salt, Na_2EDTA 6 percent. Dissolve 66.6 g Na_2EDTA in 900 ml distilled water and dilute to 1 liter with distilled water.
8. Ethylenediamine tetraacetic acid disodium salt, Na_2EDTA 2 percent. Dissolve 22.2 g Na_2EDTA in 900 ml distilled water and dilute to 1 liter with distilled water.
9. Hydrochloric acid, 12M. Reagent grade HCl.
10. Hydrochloric acid, 6M. Dilute 500 ml of the reagent grade HCl to 1 liter with distilled water.
11. Hydrochloric acid, 1.5M. Dilute 125 ml of the reagent grade HCl to 1 liter with distilled water.
12. Nitric acid, 16M. Reagent grade HNO_3.
13. Nitric acid, 6M. Dilute 375 ml of the reagent grade HNO_3 to 1 liter with distilled water.
14. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Dilute to 100 ml with distilled water. Store in brown bottle.
15. Sodium acetate, buffered pH 4.6. Dissolve 200 g of anhydrous sodium acetate in 500 ml distilled water. Adjust pH to 4.6 with acetic acid and dilute to 1 liter with distilled water.
16. Sodium carbonate. Anhydrous reagent powder.
17. Sodium carbonate, 1.5M. Dissolve 159 g of Na_2CO_3 in 900 ml of distilled water and dilute to 1 liter with distilled water.
18. Sodium chloride, 4M. Dissolve 234 g of NaCl in 900 ml of

distilled water and dilute to 1 liter with distilled water.

19. Sodium hydroxide. Reagent grade pellets.
20. Strontium carrier, 20. mg Sr^{+2}/ml. Dissolve 48.3 g of $Sr(NO_3)_2$ in 900 ml of distilled water. Add 1 ml 16M HNO_3 reagent and dilute to 1 liter with distilled water.

Procedure

1. Dry the homogenized sample at 110°C to constant weight.
2. Ash the dried sample at 550°C for no less than 72 hours.
3. Place 10 g of ash in a 250 ml nickel crucible. Add 2 ml of strontium carrier and 1 ml barium carrier to the ash. Add 1 ml of 2M calcium nitrate solution. See Note 2.
4. Add 50 g of sodium hydroxide pellets, mix and fuse over a blast burner for 15 minutes or until the sample is a clear red melt. Begin heating slowly. Gradually increase heating when reaction subsides. Remove crucible from flame and slowly add 5 g anhydrous sodium carbonate, swirl to mix, and heat the clear melt for 20 minutes.
5. Transfer the crucible from the heat to a cold water bath in order to crack the fusion mixture. Transfer the mixture to a one-liter beaker and wash the residue into the beaker with distilled water.
6. Add 200 ml hot, distilled water to the beaker and gently boil to disintegrate the fused mixture. See Note 3.
7. Transfer the sample to a 250 ml centrifuge bottle and centrifuge for five minutes. Discard supernate.
8. Wash the residue twice with 200 ml aliquots of hot distilled water, discarding the supernate each time.
9. Dissolve the residue in 20 ml 6M HCl by gently boiling until the solution is transparent. Add 100 ml water.
10. If insoluble silica is present, centrifuge, pour off supernate and save in separate beaker.
11. Wash the residue twice with 100 ml aliquots of distilled water.

Centrifuge and add wash water to beaker containing first wash solution from step 10. Discard residue.

12. Add combined sample to 500 ml of 6 percent disodium EDTA solution in a 2-liter beaker. Adjust pH to 3.8 with pH meter using approximately 10 ml 15M NH_4OH. See Note 4.
13. Stir vigorously for 75 minutes using a magnetic stirrer to precipitate the magnesium salt of EDTA.
14. Filter off any Mg EDTA and adjust filtrate to pH 4.6 (pH meter) with approximately 2 ml of 15M NH_4OH. Add 20 ml of sodium acetate buffer solution, pH 4.6 and readjust solution to pH 4.6 (pH meter) with approximately 4 ml of 15M NH_4OH. Dilute to 1 liter.
15. Transfer solution to column reservoir and let flow through the cation resin column at a flow rate of 20 ml per minute. Stop flow when just enough solution remains to cover top of resin in column.
16. Adjust pH of 600 ml, 2 percent Na_2EDTA to 5.1 with 6M NH_4OH. Add to column reservoir and let flow through column at 20 ml/minute. Record time at end of elution as beginning of yttrium-90 ingrowth.
17. Wash column with 200 ml water at a flow rate of 20 ml/minute. Discard all effluents.
18. Place 460 ml 1.5M HCl in reservoir and elute at a flow rate of 8 ml/minute. Discard first 60 ml of effluent. Collect the next 400 ml, which contains the strontium fraction.
19. Add 200 ml 15M NH_4OH to the effluent containing the strontium fraction and stir with a magnetic stirrer. Slowly add 10 ml 1.5M Na_2CO_3 solution and stir vigorously for an additional 30 minutes.
20. Collect the strontium carbonate precipitate on a tared membrane filter. Wash with three 10 ml aliquots each of water and ethanol. Transfer to a planchet and allow sample to dry one hour in a desiccator.

21. Weigh the precipitate and count the radiostrontium in a low-background beta counter. Repeat the count in six to seven days and calculate the strontium-90 from the difference in the counts.
22. Regenerate the resin column by flowing 600 ml 4M NaCl over the column, followed by 1 liter distilled water.

Calculations

Calculate the concentration, Z, of strontium-90 in picocuries per liter or picocuries per gram ash as follows:

$$Z = \frac{[A]\,[B] \; - \; [C]\,[D]}{[1+(E)(F)]\,(A) \; - \; [1+(G)(H)]\,(C)} \times \frac{1}{(2.22)(I)(J)(K)(L)}$$

where

A = decay factor of ^{89}Sr from the time of collection to the time of the first count,
B = net counts per minute of total strontium on second count,
C = decay factor of ^{89}Sr from the time of collection to the time of the second count,
D = net counts per minute of total strontium on first count,
E = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the second count,
F = ^{90}Y ingrowth factor from the time of separation to the time of the second count,
G = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the first count,
H = ingrowth factor of ^{90}Y from time of separation to time of first count,
I = counting efficiency of ^{90}Sr first count,
J = chemical yield of strontium,

K = absorption factor for ^{90}Sr, and
L = sample volume in liters or sample weight in grams.

Calculate the concentration, Z, of strontium-89 in picocuries per liter or picocuries per gram ash as follows:

$$Z = \frac{(D) - [1 + (H)(G)]\,(M)}{A} \times \frac{1}{(2.22)(O)(J)(N)(L)}$$

where

D = net counts per minute of total strontium on the first count,
H = ^{90}Y ingrowth factor from separation to first count,
G = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the first count,
M = net cpm of ^{90}Sr (first fraction of ^{90}Sr calculation),
A = decay factor of ^{89}Sr from time of collection to the time of first count,
O = absorption factor for ^{89}Sr,
J = chemical yield of strontium,
N = counting efficiency of ^{89}Sr, and
L = sample volume in liters or sample weight in grams.

Calculate the lower limit of detection (LLD) in picocuries per gram as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(T)(W)}$$

where

C_B = background count rate,
T = counting time (same for sample and background),

E = beta counter efficiency,

R = fractional chemical yield,

W = sample size (grams), and

2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is the same as the background counting time.

Notes

1. Metricel is a trademark of Gelman Sciences, Inc., Ann Arbor, Michigan.
2. For the following types of sample ash, use the weights listed instead of the 10 g in step 3 of this procedure:
    Fish ash, 3 g.
    Bone ash, 3 g. Do not add $Ca(NO_3)_2$ to bone.
    Vegetation ash, 5 g.

    For 3 g of ash use 20 g of NaOH pellets and 2 g Na_2CO_3 for fusion. For 5 g of ash use 25 g of NaOH pellets and 3 g Na_2CO_3 for fusion.
3. If the fusion mass is not easily removed from the crucible, it may be necessary to add the crucible to the boiling water to dislodge the mass.
4. If precipitation occurs, increase pH with 6M NH_4OH until clear then bring pH back to 3.8 with 6M HCl.

References

1. Porter, C.R., Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples, Public Health Service Publication No. 999-RH-10 (1965).
2. Velten, R.J., "Resolution of Sr-89 and Sr-90 in Environmental Media by an Instrumental Technique," Nuclear Instruments and Methods, 42, 169 (1966).

3. Porter, C.R., Kahn, B., Carter, M.W., Rehnberg, G.L., and Pepper, E.W., "Determination of Radiostrontium in Food and Other Environmental Samples," Environmental Science and Technology, 1, 745-750 (1967).

RADIOCHEMICAL DETERMINATION OF RADIOSTRONTIUM IN MILK

Principle

Barium and strontium carriers are added to the milk sample. Calcium in the milk is complexed with EDTA to prevent loading the cation exchange resin through which the milk is passed. A one liter sample of milk is passed through 85 ml of resin at a rate of up to 100 ml per minute. Strontium is eluted from the resin and precipitated. Strontium-89 and strontium-90 are radioassayed separately by measuring the ingrowth of yttrium-90.

Special Apparatus

1. Ion exchange column, 3.2 cm internal diameter, 15 cm in length.
2. Graduated separatory funnel as reservoir for column, 1 liter capacity.
3. Metricel DM-800 membrane filters or equivalent, 25 mm diameter, 0.8 micrometer pore size. See Note 1.
4. Stainless steel planchets, 5 cm diameter.
5. Suction filter apparatus.
6. Glassware.
7. Desiccator.
8. Floor centrifuge.
9. pH meter.

Reagents

1. Acetic acid, glacial. Reagent grade $HC_2H_3O_2$.
2. Ammonium acetate buffer, pH5. Dissolve 153 g ammonium acetate in 700 ml distilled water. Adjust pH to 5 with glacial acetic acid. Dilute to 1 liter with distilled water.
3. Ammonium acetate buffer, pH 5.2. Dissolve 153 g ammonium acetate in 700 ml distilled water. Adjust pH to 5.2 with glacial acetic acid. Dilute to 1 liter with distilled water.

4. Ammonium hydroxide, 15M. Reagent grade NH_4OH.

5. Barium carrier, 20 mg Ba^{+2}/ml. Dissolve 38.1 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16M HNO_3 and dilute to 1 liter with distilled water.

6. Cation exchange resin, Dowex 50W-X8, 50-100 mesh, Na^+ form, or equivalent. Wash 85 ml resin (H^+) with 600 ml 4M NaCl to convert resin to Na^+ form. Wash all excess NaCl from resin with water and check for chloride with 0.1M $AgNO_3$ before using resin.

7. Ethanol, 95 percent reagent.

8. Ethylenediamine tertraacetic acid complexing solution. Dissolve 216 g Na_2EDTA in 2500 ml distilled water. Add 20 ml each of strontium and barium carriers (20 mg/ml). Then add 200 ml ammonium acetate buffer, pH 5.2 and adjust pH to 5.65 with 15M ammonium hydroxide. Dilute to 3 liters.

9. Ethylenediamine tetraacetic acid disodium salt, Na_2EDTA, 3 percent. Dissolve 33.3 g of Na_2EDTA in 900 ml distilled water and dilute to 1 liter with distilled water.

10. Nitric acid, 16M. Reagent grade HNO_3.

11. Nitric acid 1M. Dilute 62 ml HNO_3 to 1 liter with distilled water.

12. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Dilute to 100 ml with distilled water. Store in brown bottle.

13. Sodium carbonate, 1.5M. Dissolve 159 g of Na_2CO_3 in 900 ml distilled water and dilute to 1 liter with distilled water.

14. Sodium chloride, 1.5M. Dissolve 87.7 g NaCl in 900 ml distilled water and dilute to 1 liter with distilled water.

15. Sodium chloride, 4M. Dissolve 234 g NaCl in 900 ml distilled water and dilute to 1 liter with distilled water.

16. Sodium chromate, 0.25M. Dissolve 40.5 g Na_2CrO_4 in 900 ml distilled water and dilute to 1 liter with distilled water.

17. Sodium hydroxide, 6M. Dissolve 240 g NaOH in 900 ml distilled water and dilute to 1 liter with distilled water.
18. Strontium carrier, 20 mg Sr^{+2}/ml. Dissolve 48.3 g $Sr(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16M HNO_3 and dilute to 1 liter with distilled water.

Procedure

1. Filter a 1 liter sample of milk through cheesecloth and add 300 ml of the complexing solution to the milk sample and mix well.
2. Adjust milk mixture to pH 5.2 with 15M NH_4OH using pH meter.
3. Pour the milk sample into a graduated separatory funnel and attach to the top of the ion exchange column.
4. Open stopcocks on reservoir and column and allow the milk to flow through the resin by gravity that will not exceed 100 ml/min.
5. After all the milk has passed through the column, rinse sides at top of column with 50 ml water and wash with approximately 200 ml water until the effluent runs clear. Do not let column run dry.
6. Add 800 ml of 3 percent Na_2EDTA (pH 5.2) to the reservoir and elute through the column at 20 ml per minute. Record the time of EDTA elution as the beginning of yttrium-90 ingrowth.
7. Add 200 ml distilled water to reservoir and run through column at 20 ml per minute.
8. Add 200 ml of 1.5M NaCl to reservoir and pass solution through the column at a flow rate of 10 ml per minute.
9. Add 1000 ml 4M NaCl to reservoir and pass solution through the column at a flow rate of 20 ml per minute. Collect the first 400 ml of eluate, which contains strontium and barium, and allow the remaining 600 ml NaCl to pass through the column to regenerate the resin.
10. Wash all excess NaCl from resin with distilled water and check eluate for chloride with 0.1M $AgNO_3$ before reusing resin.

11. Add 1 ml of 6M NaOH to the 400 ml of eluate from step 9. Stir and slowly add 10 ml of 1.5M Na_2CO_3 to precipitate $SrCO_3$. Continue vigorous stirring for 30 minutes using a magnetic stirrer.
12. Transfer one half of the contents to a 250 ml centrifuge bottle. Centrifuge at 2000 rpm for 10 minutes and carefully pour off and discard supernate.
13. Add the remaining solution to the precipitate in the 250 ml centrifuge bottle. Centrifuge at 2000 rpm for 10 minutes. Pour off and discard supernate.
14. Place the centrifuge bottle containing the precipitate in a hot water bath held at 70°C.
15. Add 5 ml 1M HNO_3 to centrifuge bottle to dissolve precipitate. Transfer solution to a 50 ml centrifuge tube.
16. Wash the 250 ml centrifuge bottle with 5 ml of ammonium acetate buffer, pH5, and add the wash to the dissolved precipitate in the 50 ml centrifuge tube.
17. Heat the 50 ml centrifuge tube at 70°C in a water bath with stirring and slowly add 1 ml of 0.25M Na_2CrO_4 to precipitate barium chromate.
18. Cool tube from step 17 in ice bath, centrifuge and decant supernate containing strontium into another 50 ml centrifuge tube. Discard barium chromate precipitate.
19. Add 2 ml 15M NH_4OH to the supernate with stirring and precipitate strontium carbonate by adding 2 ml 1.5M Na_2CO_3.
20. Stir precipitate for ten minutes. Centrifuge for five minutes. Pour off and discard supernate.
21. Add 20 ml of distilled water to tube to wash the precipitate. Centrifuge and discard wash solution. Take up precipitate in 10 ml distilled water. Gently swirl to break up precipitate.
22. Filter sample through a tared membrane filter. Wash with three 10 ml aliquots each of water and ethanol.

23. Dry sample for one hour in a desiccator, weigh and count in a low background beta counter.
24. Recount sample in six to seven days.

Calculations

Calculate the concentration, Z, of strontium-90 in picocuries per liter or picocuris per gram ash as follows:

$$Z = \frac{[A]\,[B] \; - \; [C]\,[D]}{[1+(E)(F)]\,(A) \; - \; [1+(G)(H)]\,(C)} \times \frac{1}{(2.22)(I)(J)(K)(L)}$$

where

A = decay factor of ^{89}Sr from the time of collection to the time of the first count,
B = net counts per minute of total strontium on second count,
C = decay factor of ^{89}Sr from the time of collection to the time of the second count,
D = net counts per minute of total strontium on first count,
E = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the second count,
F = ^{90}Y ingrowth factor from the time of separation to the time of the second count,
G = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the first count,
H = ingrowth factor of ^{90}Y from time of separation to time of first count,
I = counting efficiency of ^{90}Sr first count,
J = chemical yield of strontium,
K = absorption factor for ^{90}Sr, and
L = sample volume in liters or sample weight in grams.

Calculate the concentration, Z, of strontium-89 in picocuries per liter or picocuries per gram ash as follows:

$$Z = \frac{(D) - [1 + (H)(G)](M)}{A} \times \frac{1}{(2.22)(O)(J)(N)(L)}$$

where

D = net counts per minute of total strontium on the first count,
H = ^{90}Y ingrowth factor from separation to first count,
G = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the first count,
M = net cpm of ^{90}Sr (determined by ^{90}Sr calculation),
A = decay factor of ^{89}Sr from time of collection to the time of first count,
O = absorption factor for ^{89}Sr,
J = chemical yield of strontium,
N = counting efficiency of ^{89}Sr, and
L = sample volume in liters or sample weight in grams.

Calculate the lower limit of detection (LLD) in picocuries per gram as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(T)(V)}$$

where

C_B = background count rate,
T = counting time (same for sample and background),
E = beta counter efficiency,
R = fractional chemical yield,
V = sample size (liters), and
2.22 = dpm per pCi,

This LLD calculation is valid if the sample counting time is the same as the background counting time.

Notes

1. Metricel is a trademark of Gelman Sciences Inc., Ann Arbor, Michigan.

References

1. Porter, C.R., Cahill, D., Schneider, R., Robbins, P., Perry, W., and Kahn, B., "Determination of Strontium-90 in Milk by an Ion Exchange Method," Analytical Chemistry, 33, 1306-1308 (1961).
2. Porter, C.R. and Kahn, B., "Improved Determination of Strontium-90 in Milk by an Ion Exchange Method," Analytical Chemistry, 36, 676-8, (1964).
3. Porter, C., Carter, M. W., Kahn, B. and Pepper, E. W., Rapid Field Method for the Collection of Radionuclides in Milk Proceedings of the First International Congress of Radiation Protection, Rome, Italy September 5-10, 1966.
4. Velten, R. J., "Resolution of Sr-89 and Sr-90 in Environmental Media by an Instrumental Technique," Nuclear Instruments and Methods, 42, 1969 (1966).
5. Rehnberg, G.L., Strong, A.B., Porter, C.R., and Carter, M.W., "Levels of Stable Strontium in Milk and the Total Diet," Environmental Science and Technology, 3, 171-173 (1969).

RADIOCHEMICAL DETERMINATION OF STRONTIUM-90 IN URINE

Principle

Yttrium carrier in a citric acid solution is added to the urine sample. The sample is passed over an anion exchange resin after adjusting the pH to 4.5. Yttrium is eluted from the resin column with HCl and is precipitated as yttrium oxalate. The yttrium-90 is radioassayed on a low-background beta counter and the activity of strontium-90 is calculated.

Special Apparatus

1. Centrifuge.
2. Ion exchange column, 3.8 cm dia., 18 cm length.
3. pH meter.
4. Separatory funnel, 1 liter capacity.
5. Suction filter apparatus for 25 mm membrane filter.
6. Metricel DM 800 filter membranes or equivalent, 25 mm diameter, 0.8 micrometer pore size. See Note 1.

Reagents

1. Ammonium hydroxide, 15M, reagent grade NH_4OH.
2. Anion exchange resin. Dowex 1X8 or equivalent 50-100 mesh, chloride form.
3. Citric acid, 1M, pH 4.5. Dissolve 210 g of reagent grade citric acid monohydrate in 500 ml distilled water. Adjust solution to pH 4.5 with 12M NaOH using a pH meter. Dilute the solution to 1 liter.
4. Ethanol, 95 percent reagent.
5. Hydrochloric acid, 12M, 37 percent HCl reagent.
6. Hydrochloric acid, 3M. Dilute 250 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
7. Merthiolate solution, 0.1 percent. Dissolve 1 g sodium merthiolate in 1 liter distilled water.

8. Oxalic acid, 1M. Dissolve 126 g of $C_2H_2O_4 \cdot 2H_2O$ in 900 ml of distilled water and dilute to 1 liter.
9. Sodium hydroxide, 12M. Dissolve 480 g reagent grade NaOH in 400 ml distilled water. When cool dilute to 1 liter.
10. Yttrium carrier, 10 mg Y^{+3}/ml. Heat, but avoid boiling, 12.7 g Y_2O_3 in 50 ml 16M HNO_3 until dissolved. Transfer to a 1 liter volumetric flask and dilute to 900 ml. Adjust to pH2 with 15M NH_4OH and dilute to 1 liter.

Procedure

1. Prior to sample collection, add 80 ml of merthiolate to one gallon sample container. At end of collection period (T_1) store sample for 10-14 days for yttrium-90 ingrowth.
2. Measure a 1-liter aliquot into a beaker. Add 1 ml of yttrium carrier to 5 ml of 1M citric acid in a tube. Swirl to mix and transfer quantitatively to the urine in the beaker with distilled water. Stir well.
3. Adjust to pH 4.5-5.0 with NaOH using pH meter. Filter through Whatman number 42 filter paper in a 20-cm diameter Buchner funnel with vacuum. Discard filter.
4. Transfer filtrate to a 1-liter separatory funnel and attach to the anion resin column, which is filled with distilled water.
5. Record the time (T_2). Allow sample to flow through the resin at 10 ml per minute. Discard the effluent.
6. Add 500 ml of distilled water to the separatory funnel and resume flow at 10 ml per minute. Stop flow when just enough water remains in the column to cover the resin.
7. Add 500 ml 3M HCl to the separatory funnel and let flow at 2-3 ml per minute. Discard effluent until pH drops to 2 (check with pH paper). Collect the next 65 ml of eluate in a 250 ml centrifuge bottle.
8. Allow remaining acid to pass through the column to recharge the

resin. Stir the resin bed well and wash with 500 ml distilled H_2O.

9. Centrifuge the 65 ml of eluate and transfer supernate to another centrifuge bottle. Discard any precipitate.
10. Add 2 ml of 2M oxalic acid to the eluate and adjust to pH 1.6 with 15M NH_4OH (use pH meter). Heat in a hot water bath for 15 minutes; then allow to cool to room temperature.
11. Centrifuge and discard the supernate. Wash the precipitate with 10 ml distilled water, centrifuge, and discard supernate.
12. Weigh a stainless steel planchet and 2.5-cm diameter membrane filter. Place filter in filtering apparatus.
13. Transfer precipitate to filter membrane with distilled water. Wash with 15 ml distilled water and 30 ml of ethanol. Continue suction for two minutes.
14. Transfer the filter with precipitate to the stainless steel planchet and weigh the sample to determine yttrium recovery.
15. Count in a low-background beta counter and record the time (T_3). Count again after three days to confirm absence of contamination of yttrium-90 by other radionuclides.

Calculations

Calculate the concentration, Z, of strontium-90 in picocuries per 24 hour sample as follows:

$$Z = \frac{(C_1 - C_B)(V_1)}{(A)(B)(E)(F)(V_2)}$$

where

C_1 = sample gross counts per minute,
C_B = counter background counts per minute,
V_1 = volume of 24-hour sample in liters,

A = correction factor for ^{90}Y decay ($e^{-\lambda t}$) where t (hours) is the time from beginning of analysis to time of counting (T_3-T_2),

B = correction factor for ingrowth of ^{90}Y ($1-e^{-\lambda t}$) where t (hours) is the time from the end of sample collection period to time of beginning of analysis (T_2-T_1),

E = counter efficiency for ^{90}Y in cpm/pCi,

F = yttrium oxalate recovery, and

V_2 = aliquot analyzed (liters).

Calculate the lower limit of detection (LLD) for strontium-90 in picocuries per 24-hour sample as follows:

$$LLD = \frac{4.66\sqrt{C_B T} \quad V_1}{(A)(B)(E)(F)(V_2)(T)}$$

where

C_B = counter background counts per minute,

V_1 = volume of 24-hour sample in liters,

A = correction factor for ^{90}Y decay ($e^{-\lambda t}$) where t (hours) is the time from begining of analysis to time of counting,

B = correction factor for ingrowth of ^{90}Y ($1-e^{-\lambda t}$) where t (hours) is the time from the end of sample collection period to time of beginning of analysis,

E = counter efficiency for ^{90}Y in cpm/pCi,

F = yttrium oxalate recovery, and

V_2 = aliquot analyzed (liters).

This LLD is valid only of the background counting time is equal to the sample counting time.

Notes

1. Metricel is a trademark of Gelman Sciences Inc., Ann Arbor, MI.

References

1. Cahill, D.F., and Lindsey, G.I., "Determination of Strontium-90 in Urine by Anion Exchange," Analytical Chemistry, 38, 639 (1966).

RADIOCHEMICAL DETERMINATION OF RADIOSTRONTIUM IN WATER, SEA WATER AND OTHER AQUEOUS MEDIA

Principle

Barium, calcium and strontium carriers are added to the sample. Magnesium is precipitated and removed from the sample at pH 3.8. Barium and strontium are adsorbed on a cation exchange resin while calcium is eluted. Barium and strontium are selectively eluted and strontium is precipitated. Strontium-89 and strontium-90 are radioassayed separately by measuring ingrowth of yttrium-90. Urine samples are analyzed for strontium using a different procedure. See Strontium-90 in Urine.

Special Apparatus

1. Graduated separatory funnel as reservoir for column, 1 liter capacity.
2. Ion exchange column, 2.5 cm internal diameter, 18 cm long.
3. Metricel DM 800 membrane filters or equivalent, 25 mm diameter, 0.8 micrometer pore size. See Note 1.
4. Stainless steel planchets, 5 cm diameter.
5. Suction filter apparatus.
6. Glassware.
7. Whatman 2V fluted filter paper or equivalent.
8. Magnetic stirrer and stirring bars.

Reagents

1. Acetic acid, glacial. Reagent grade $HC_2H_3O_2$.
2. Ammmonium hydroxide, 15$\underline{M}$. Reagent grade NH_4OH.
3. Ammonium hydroxide, 6$\underline{M}$. Dilute 400 ml NH_4OH reagent to 1 liter with distilled water.
4. Barium carrier, 20 mg Ba^{+2}/ml. Dissolve 38.2 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16$\underline{M}$ HNO_3 and dilute to 1 liter with distilled water.

5. Barium carrier, 5 mg Ba^{+2}/ml. Dissolve 9.5 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16M HNO_3 and dilute to 1 liter with distilled water.
6. Calcium nitrate, 2M. Dissolve 47.2 g $Ca(NO_3)_2 \bullet 4H_2O$ in distilled water and dilute to 100 ml with distilled water.
7. Cation exchange resin. Dowex 50WX8, 50-100 mesh, Na^+ form, 40 ml per column. Wash resin (H^+) with 600 ml 4M NaCl to convert resin to Na^+ form. Wash all excess NaCl from resin with water and check effluent wash water for chloride with 0.1M $AgNO_3$ before using resin.
8. Ethanol, 95 percent reagent.
9. Ethylenediamine tetraacetic acid, disodium salt. Na_2EDTA reagent powder.
10. Ethylenediamine tetraacetic acid, disodium salt, Na_2EDTA, 3 percent. Dissolve 33.3 g of Na_2 EDTA in 900 ml distilled water and dilute to 1 liter with distilled water.
11. Ethylenediamine tetraacetic acid, disodium salt, Na_2EDTA, 2 percent. Dissolve 22.2 g of Na_2 EDTA in 900 ml distilled water and dilute to 1 liter with distilled water.
12. Hydrochloric acid, 12M. Reagent grade HCl.
13. Hydrochloric acid, 6M. Dilute 500 ml reagent grade HCl to 1 liter with distilled water.
14. Hydrochloric acid, 1.5M. Dilute 125 ml reagent grade HCl to 1 liter with distilled water.
15. Nitric acid, 16M. Reagent grade HNO_3.
16. Silver nitrate, 0.1M. Dissolve 1.7g $AgNO_3$ reagent in distilled water. Add 1 ml 16M HNO_3 and dilute to 100 ml with distilled water. Store in brown bottle.
17. Sodium acetate buffer, pH 4.6. Dissolve 200 g $NaC_2H_3O_2$ in 400 ml distilled water. Adjust pH to 4.6 with glacial acetic acid. Dilute to 1 liter with distilled water.

18. Sodium carbonate, 1.5M. Dissolve 159 g of Na_2CO_3 in 900 ml distilled water and dilute to 1 liter with distilled water.
19. Sodium chloride, 4M. Dissolve 234 g of NaCl in 900 ml distilled water and dilute to 1 liter with distilled water.
20. Sodium hydroxide, 6M. Dissolve 240 g of NaOH in 900 ml distilled water and dilute to 1 liter with distilled water.
21. Strontium carrier, 20 mg Sr^{+2}/ml. Dissolve 48.3 g $Sr(NO_3)_2$ in 900 ml water. Add 1 ml 16M HNO_3 and dilute to 1 liter with distilled water.

Procedure

1. Acidify a 3.78 liter (one gallon) sample with 2 ml of 6M HCl.
2. Mix thoroughly and filter through a fluted filter paper.
3. Place a one liter aliquot of the sample in a 2 liter beaker.
4. Add 2 ml of strontium carrier, 1 ml of barium carrier and 2 ml of calcium nitrate solution. Stir well.
5. For fresh water samples, proceed to step 6; for sea water samples, pretreat as directed in steps 5 a through 5 g.
   (a) Heat sample to near boiling on a hot plate.
   (b) Adjust pH to 10 with approximately 10 ml of 6M NaOH.
   (c) Add 30 ml of 1.5M Na_2CO_3 with stirring.
   (d) Continue heating until precipitate settles to the bottom of the beaker.
   (e) Remove sample from the hot plate and allow solution to cool to room temperature.
   (f) Decant supernate. Transfer precipitate to a 250 ml centrifuge bottle with distilled water. Centrifuge and discard supernate.
   (g) Dissolve precipitate in 30 ml of 6M HCl and add to 500 ml of 3 percent disodium EDTA. Go to step 7.
6. Add 33.3 g disodium EDTA powder to the fresh water sample from step 5 and stir until dissolution of the powder is complete.

7. Adjust sample to pH 3.8 with pH meter using 15M NH_4OH or 6M HCl.
8. Stir vigorously for 75 minutes using a magnetic stirrer to precipitate the magnesium salt of EDTA.
9. Filter, if necessary, and adjust filtrate to pH 4.6 with approximately 2 ml of 15M NH_4OH.
10. Add 20 ml of sodium acetate buffer solution, pH 4.6 and readjust to pH 4.6 with approximately 4 ml of 15M NH_4OH.
11. Pass the 1-liter sample through resin column at 20 ml per minute. Stop the flow when enough solution remains to cover resin.
12. Adjust 600 ml of the 2 percent disodium EDTA to pH 5.1 with 6M NH_4OH.
13. Place the 2 percent disodium EDTA from step 12 in the column reservoir and let flow through the resin column at 20 ml per minute.
14. Record time at end of elution in step 13 as beginning of yttrium-90 ingrowth.
15. Wash the column with 200 ml water at a flow rate of 20 ml per minute and discard all effluents.
16. Place 460 ml 1.5M HCl in reservoir and elute at a flow rate of 8 ml per minute, discarding the first 60 ml of effluent.
17. Collect the next 400 ml, which contain the strontium fraction.
18. Add 200 ml 15M NH_4OH to the strontium fraction from step 17 and stir with a magnetic stirrer. Slowly add 10 ml 1.5M Na_2CO_3 solution and stir vigorously for 30 minutes.
19. Collect the strontium carbonate precipitated in step 18 on a weighed membrane filter. Wash with three 10 ml aliquots each of water and ethanol. Transfer to a planchet and dry for 1 hour in a desiccator.
20. Weigh the strontium carbonate to the nearest 0.1 mg and count the radiostrontium in a low-background beta counter.
21. Count the sample again after six to seven days and calculate the strontium-90.

22. Regenerate the cation exchange resin by eluting 600 ml of 4M NaCl through the column at 8 ml/minute. Wash the resin with water until all chlorides are removed by checking with a silver nitrate solution.

Calculations

Calculate the concentration, Z, of strontium-90 in picocuries per liter or picocuries per gram ash as follows:

$$Z = \frac{[A]\,[B] - [C]\,[D]}{[1+(E)(F)]\,(A) - [1+(G)(H)]\,(C)} \times \frac{1}{(2.22)(I)(J)(K)(L)}$$

where

A = decay factor of ^{89}Sr from the time of collection to the time of the first count,
B = net counts per minute of total strontium on second count,
C = decay factor of ^{89}Sr from the time of collection to the time of the second count,
D = net counts per minute of total strontium on first count,
E = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the last count,
F = ^{90}Y ingrowth factor from the time of separation to the time of the last count,
G = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the first count,
H = ingrowth factor of ^{90}Y from time of separation to time of first count,
I = counting efficiency of ^{90}Sr first count,
J = chemical yield of strontium,
K = absorption factor for ^{90}Sr, and
L = sample volume in liters or sample weight in grams.

Calculate the concentration, Z, of strontium-89 in picocuries per liter or picocuries per gram ash as follows:

$$Z = \frac{(D) - [1 + (H)(G)]\,(M)}{A} \times \frac{1}{(2.22)(O)(J)(N)(L)}$$

where

D = net counts per minute of total strontium on the first count,
H = ^{90}Y ingrowth factor from separation to first count,
G = ratio of the ^{90}Y/^{90}Sr counting efficiencies on the first count,
M = net cpm of ^{90}Sr (first fraction of ^{90}Sr calculation),
A = decay factor of ^{89}Sr from time of collection to the time of first count,
O = absorption factor for ^{89}Sr,
J = chemical yield of strontium,
N = counting efficiency of ^{89}Sr, and
L = sample volume in liters or sample weight in grams.

Calculate the lower limit of detection (LLD) in picocuries per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(T)(V)}$$

where

C_B = background count rate,
T = counting time (same for sample and background),
2.22 = dpm per pCi,
E = beta counter efficiency,
R = fractional chemical yield, and
V = sample size (liters).

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. Metricel is a trademark of Gelman Sciences, Inc., Ann Arbor, Michigan.

References

1. Porter, C.R., Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples, Public Health Service Publication No. 999-RH-10 (1965).
2. Velten, R.J., "Resolution of Sr-89 and Sr-90 in Environmental Media by an Instrumental Technique," Nuclear Instruments and Methods, 42, 169 (1966).
3. Porter, C.R., Kahn, B., Carter, M.W., Rehnberg, G.I., and Pepper, E.W., "Determination of Radiostrontium in Food and Other Environmental Samples," Environmental Science and Technology, 1, 745-750 (1967).

PREPARATION OF THORIUM-234 TRACER SOLUTION

Principle

Uranium is adsorbed on an anion exchange resin in strong HCl. The thorium-234 decay product is periodically eluted with strong HCl. The eluted thorium is further purified by passing the eluted solution through a second column of anion exchange resin. The final thorium-234 solution is radioassayed by coprecipitation with lanthanum as fluoride and beta counted. The solution is also checked for uranium contamination by coprecipitation for uranium with lanthanum as fluoride. The coprecipitate is radioassayed by alpha spectroscopy.

Special Apparatus

1. Ion exchange columns, 5 cm internal diameter, 15 cm length; 2.5 cm internal diameter, 14 cm length.
2. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
3. Planchets, stainless steel, 32 mm diameter.
4. Separatory funnels, 250 ml capacity as reservoirs for the ion exchange columns.
5. Suction filter apparatus for 25 mm membrane.
6. Plastic graduated cylinder, 100 ml volume.
7. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump and chamber.

Reagents

1. Anion exchange resin. Dowex 1X8, 100-200 mesh, chloride form.
2. Ethanol, 95 percent reagent.
3. Hydrochloric acid, 12M, 37 percent HCl reagent.
4. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.

5. Hydrofluoric acid, 29M, 48 percent HF reagent.
6. Hydrofluoric acid, 3M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduated cylinder and storage bottle.
7. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g high purity $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1M HCl.
8. Titanium trichloride, 20 percent reagent grade.
9. Titanium trichloride, 0.4 percent. Dilute 1 ml of the 20 percent $TiCl_3$ to 50 ml with 1 M HCl. Prepare fresh daily.
10. Uranyl acetate or other uranium salt. Reagent grade crystals.

Procedure

1. Slurry the anion exchange resin with distilled water in a beaker and fill both columns to within 2 cm from the top of the column.
2. Place the reservoirs on top of the columns and wash the resin by passing 200 ml water through the columns. Always maintain a level of liquid above the top of the resin bed.
3. Pass 300 ml of 12M HCl through the larger column at the rate of approximately 5 ml per minute.
4. Dissolve the uranium salt in 300 ml of 12M HCl and pass this solution through the larger column.
5. Pass 300 ml 12M HCl through the larger column following the uranium solution.
6. Discard the eluate and record the date the acid was passed through the resin.
7. In approximately 14 days, pass 300 ml 12M HCl through the column with the adsorbed uranium at a rate of 3 ml/minute . Collect the eluate containing the thorium-234. See Note 2.
8. Pass 200 ml 12M HCl through the smaller column at a rate of 5 ml/minute. Discard the eluate.
9. Pass the eluate from the larger column (step 7) through the second column at a rate of 3 ml/minute.

10. Wash the second column with 100 ml 12M HCl, collecting the total eluate.
11. Evaporate the total acid solution just to dryness.
12. Dissolve in 250 ml 1M HCl and filter into a storage bottle.
13. Remove at least four 1 ml aliquots of the thorium-234 tracer solution, transfer to 100 ml beakers and evaporate to dryness.
14. Add 15 ml 1M HCl to the residue in each beaker and warm to approximately 50°C.
15. Add 1 ml of lanthanum carrier and 5 ml of 3M HF to each sample. Mix well and set aside for 30 minutes.
16. Using suction, filter coprecipitated samples through filter membranes.
17. Rinse each sample beaker with 10 ml water and add to filter funnel. Rinse each beaker with 10 ml ethanol and add to funnel.
18. Remove clamp and top of funnel with suction on. Allow membrane to dry.
19. Mount individual membrane carefully on 32 mm planchet using double stick tape.
20. Count each coprecipitated sample for thorium-234 on a beta counter.
21. Each batch of thorium-234 coming from the uranium column in step 7 should be checked for uranium contamination by evaporating a 1 ml aliquot and coprecipitating for uranium in the following manner.
22. Add 15 ml 1M HCl to the residue from step 21 and warm to approximately 50°C.
23. Add 1 ml of 0.4 percent $TiCl_3$ to reduce the uranium.
24. Add 1 ml of the lanthanum carrier and 5 ml of 3M HF. Mix well and set aside for 30 minutes.
25. Using suction, filter coprecipitated sample through a filter membrane.

26. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
27. Remove clamp and top of funnel with suction on. Allow membrane to dry.
28. Mount membrane carefully on 32 mm planchet using double stick tape.
29. Count sample for 1000 minutes on alpha spectrometer. See Note 3.

Notes

1. Nuclepore is a trademark of Nuclepore Corp., Pleasanton, CA.
2. The thorium-234 should be removed from the uranium-containing column every 14 days regardless of need. Longer periods of time between elutions result in the appearance of small quantities of thorium-230 in the eluate.
3. If uranium is in the tracer solution, it must be removed by further treatment with anion exchange resin before use.

References

1. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Labatory, U.S. Department of Energy, New York.

PREPARATION OF URANIUM-232 TRACER SOLUTION

Principle

Uranium-232 has a half-life of 72 years and decays to thorium-228, which has a half-life of 1.9 years. In order to prevent contamination of samples with thorium-228 and its decay products, any stock of uranium-232 must be periodically decontaminated before use This should be done on an annual basis.

Uranium-232 is extracted into triisooctylamine (TIOA). The TIOA is washed with a mixture of HCl and HF for decontamination. Uranium is stripped from the TIOA with dilute nitric acid and wet ashed. Aliquots of the cleaned uranium tracer are coprecipitated with lanthanum flouride and radioassayed by alpha spectroscopy to determine the specific activity of the tracer solution.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Planchets, stainless steel, 32 mm diameter.
3. Plastic graduated cylinder.
4. Separatory funnels, 1 liter capacity.
5. Suction filter apparatus for 25 mm membrane.
6. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump and chamber.

Reagents

1. Ascorbic acid, crystalline reagent.
2. Ethanol, 95 percent reagent.
3. Hydrochloric acid, 12 M. 37 percent HCl reagent.
4. Hydrochloric acid, 9 M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.

5. Hydrochloric acid, 3 M/Hydrofluoric acid, 0.1 M mixture. Dilute 250 ml of the 37 percent reagent grade HCl and 3.5 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Store in a plastic bottle.
6. Hydrochloric acid, 1 M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
7. Hydrofluoric acid, 29 M. 48 percent HF reagent.
8. Hydrofluoric acid, 3 M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduated cylinder and storage bottle.
9. Hydrogen peroxide, 50 percent reagent grade.
10. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0799 g $La(NO_3)_3 \bullet 6H_2O$ per 250 ml 1 M HCl.
11. Nitric acid, 16 M. 70 percent HNO_3 reagent.
12. Nitric acid, 0.1 M. Dilute 6 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
13. Titanium trichloride, 20 percent reagent grade.
14. Titanium trichloride, 0.4 percent. Dilute 1 ml of the 20 percent $TiCl_3$ to 50 ml with distilled water. Prepare fresh daily.
15. Triisooctylamine (TIOA), reagent grade.
16. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml of the triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
17. p-Xylene, reagent grade.

Procedure

1. From the specific activity of the uranium-232 stock solution, determine the size of the aliquot to be used so that when diluted it will result in a final solution of approximately 1 pCi ^{232}U/ml.
2. Evaporate the aliquot of ^{232}U to dryness in a beaker.
3. Add 10 ml of 12 M HCl and evaporate to dryness.
4. Add 100 ml 9 M HCl to the beaker and warm to 50°C.

5. Add 10 drops of 50 percent hydrogen peroxide to the solution.
6. Equilibrate 100 ml of the 10 percent TIOA solution with 50 ml of warm 9 M HCl by shaking in a separatory funnel for one minute.
7. Allow the layers to separate and discard the lower aqueous acid phase.
8. Add the solution from step 5 to the TIOA in the separatory funnel and shake funnel for two minutes.
9. Allow phases to separate and discard the lower aqueous acid phase.
10. Wash the TIOA solution with 50 ml 9 M HCl warmed to 50°C. Shake for one minute and discard lower aqueous acid phase when separated.
11. Wash the TIOA solution with 75 ml of 3 M HCl/0.1 M HF warmed to 50°C. Shake funnel for two minutes and discard lower acid phase when separated. Repeat this step.
12. Strip the uranium tracer from the TIOA solution by adding 100 ml 0.1 M HNO_3 to the separatory funnel and shaking the funnel for two minutes.
13. Allow phases to separate; withdraw and save lower acid phase.
14. Repeat steps 12 and 13 and combine strip solutions.
15. Place combined strip solutions in clean separatory funnel.
16. Add 100 ml p-xylene to combined strip solution and shake funnel for one minute.
17. Allow phases to separate cleanly; withdraw lower aqueous acid layer into a beaker. Discard p-xylene.
18. Evaporate solution from step 17 to dryness. Do not overheat.
19. Add 10 ml 12 M HCl to residue in beaker and take to dryness. Do not overheat.
20. Take up solution in 250 ml 1 M HCl and filter through a filter membrane using suction.
21. Coprecipitate 1 ml aliquots of the stock solution in step 20 by adding each aliquot to 15 ml 1 M HCl in a beaker.
22. Add 50 mg ascorbic acid to each beaker.

23. Add 1 ml 0.4 percent $TiCl_3$ to reduce uranium.
24. Add 1 ml of lanthanum carrier and 5 ml of 3 M HF. Mix well and set aside for 30 minutes to precipitate LaF_3 carrying uranium.
25. Using suction, filter coprecipitated sample through a filter membrane.
26. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
27. Remove clamp and top of funnel with suction on. Allow membrane to dry.
28. Mount membrane carefully on 32 mm planchet using double stick tape.
29. Count sample for 1000 minutes on alpha spectrometer.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.

References

1. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.

RADIOCHEMICAL DETERMINATION OF GROSS ALPHA AND GROSS BETA PARTICLE ACTIVITY IN WATER

The water sample is evaporated onto a stainless steel planchet and counted for gross activity. This procedure provides a rapid screening measurement to indicate whether specific analyses are required.

Special Apparatus

1. Conductivity meter.
2. Hot plates.
3. Drying lamps.
4. Stainless steel planchets, 5 cm diameter.
5. Pleated filter paper, 32 mm diameter.
6. Muffle furnace.

Procedure

If some samples require separating the dissolved solids from the undissolved solids, acidify with HNO_3 and--

1. Filter the water sample with pleated filter paper. Dry and ash filter paper at 500°C for 12 to 24 hours.
2. Determine the dissolved solid content of the filtrate by measuring the conductivity and determining the solids from Figure 1. This is to determine the volume to be evaporated. The maximum sample thickness should be less than $5 mg/cm^2$ (on 20 cm^2 area, i.e. 100 mg).
3. Transfer the specific volume of water to a beaker and evaporate to a small volume on a hot plate. Avoid dryness.
4. Transfer residue from beaker to a tared stainless steel planchet using a rubber policeman and as little distilled water as possible.
5. Dry under a heat lamp, flame over a burner until dull red, cool, weigh and store in a desiccator. See Note 1.
6. Count for gross alpha and gross beta particle activity.
7. Repeat steps 4, 5, and 6 for the ash, if necessary.

Calculations

Calculate the concentration, Z, of gross alpha or beta in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(A)(V)(F)}$$

where

C_1 = sample counts per minute,
C_B = background counts per minute,
A = counting efficiency for natural uranium,
V = sample volume (liters),
F = self absorption factor from Table 1 or Table 2 based on dry sample weight, and
2.22 = dpm per pCi.

Calculate the lower limits of detection (LLD) as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(A)(V)(F)(T)}$$

where

C_B = background counts per minute,
T = counting time,
A = counting efficiency for natural uranium,
V = sample volume (liters),
F = self-absorption factor from Table 1 or 2 based on sample weight, and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

TABLE 1

Alpha Particle Absorption Factor vs Sample Weight

Sample Weight, mg	Alpha Absorption Factor
0	1.0
5	.95
10	.90
15	.84
20	.79
25	.74
30	.69
35	.64
40	.59
45	.55
50	.50
55	.45
60	.42
65	.40
70	.38
75	.36
80	.35
90	.34
100	.33
110	.32
120	.30
130	.29
140	.28
150	.27
160	.27

TABLE 2

Beta Particle Absorption Factor vs Sample Weight

Sample Weight, mg*	Beta Absorption Factor
less than 40	1.000
40	.989
45	.982
50	.975
55	.968
60	.961
65	.954
70	.947
75	.940
80	.933
85	.926
90	.919
95	.912
100	.905

* For sample thickness, mg/cm^2, on 5 cm dia. planchet, divide sample weight by 20.

Notes

1. Flaming the planchet will result in the loss of polonium-210, if present.

References

1. Analysis of Radionuclides in Water. Training Course Manual, U.S. Department of Health, Education, and Welfare, Public Health Service (1965).

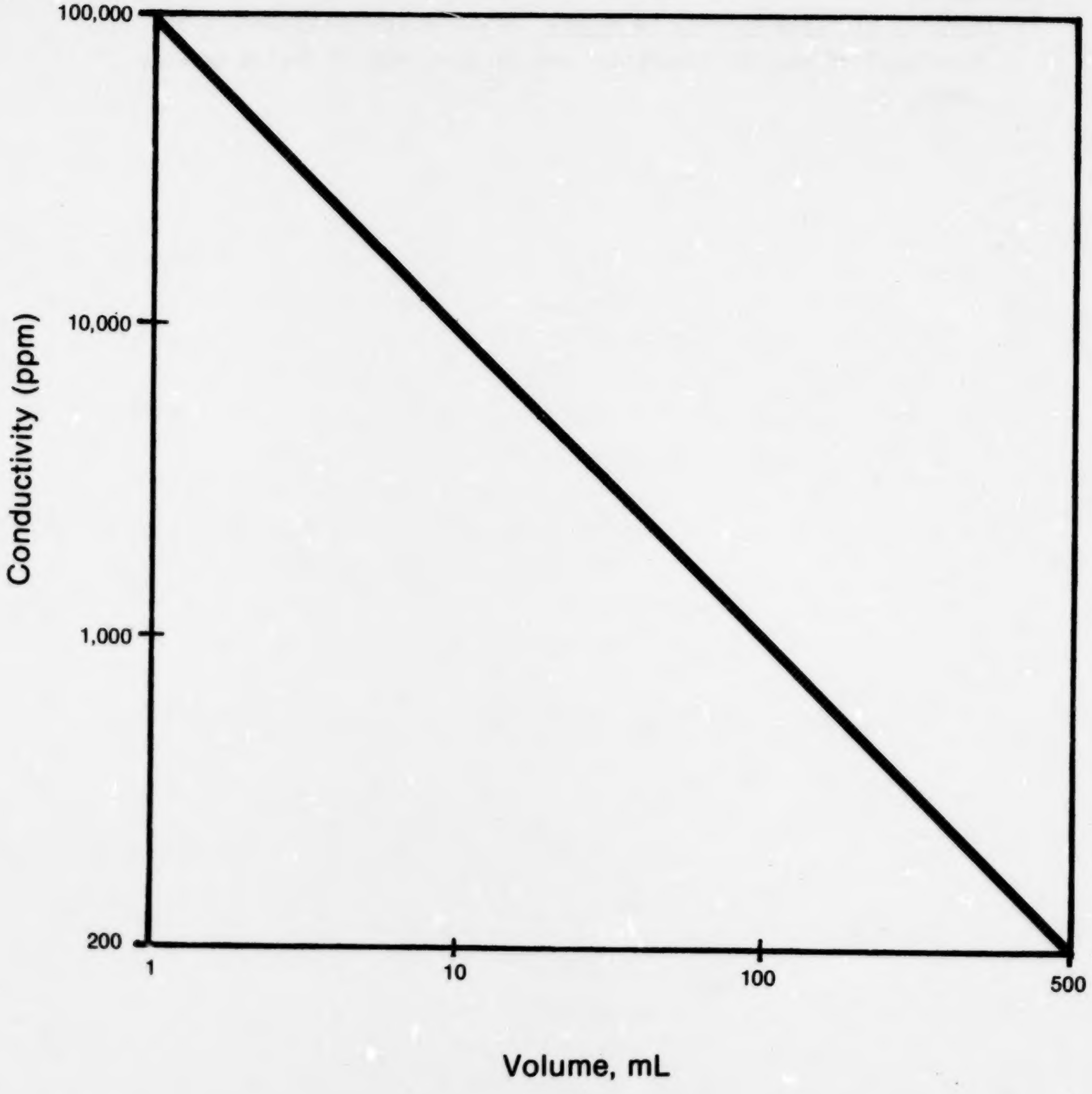

Figure 1. **Conductivity vs. volume.**

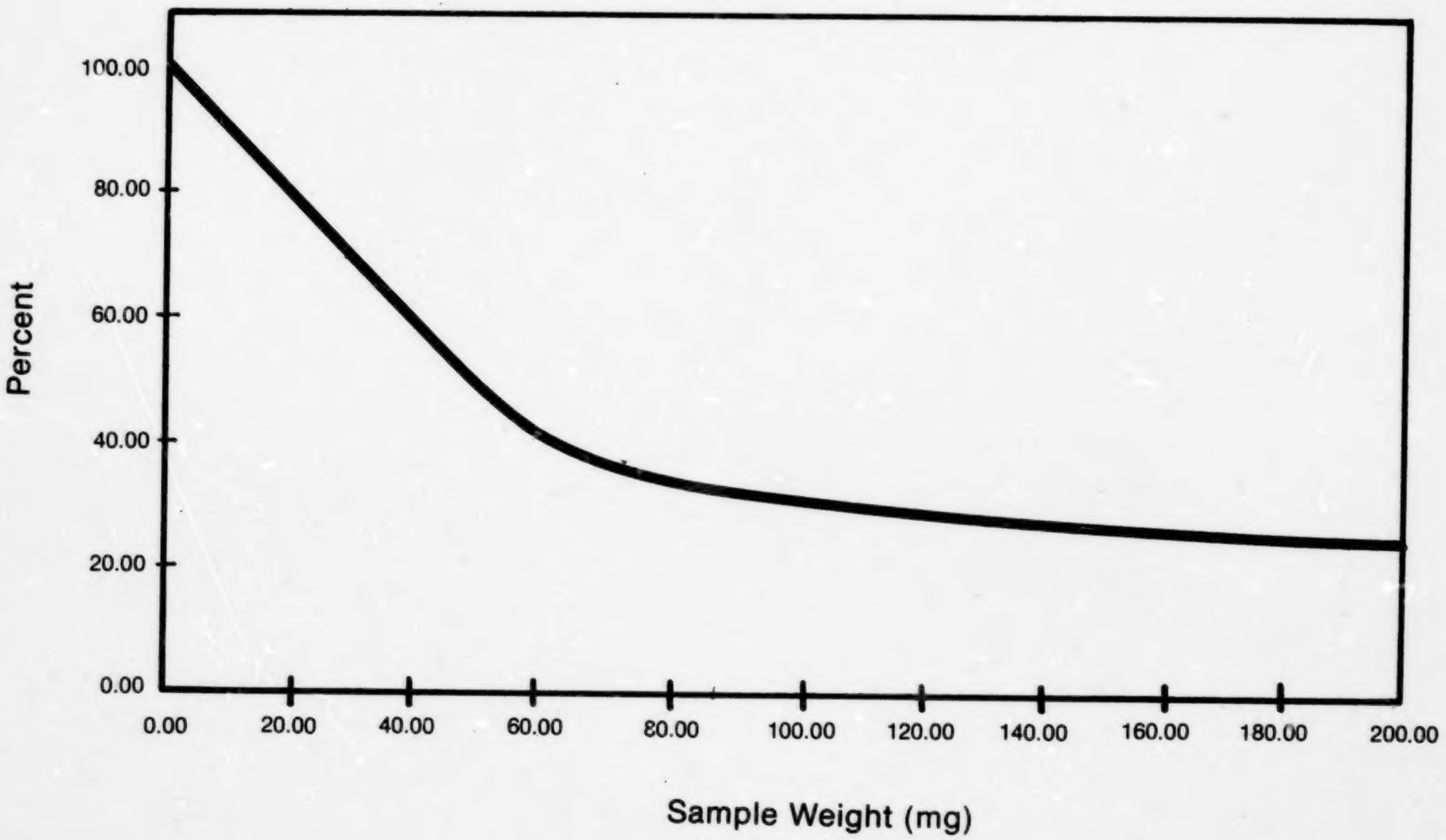

Figure 2. Gross alpha self-absorption vs. sample weight.

RADIOCHEMICAL DETERMINATION OF GROSS ALPHA ACTIVITY IN DRINKING WATER BY COPRECIPITATION

Principle

An aliquot of drinking water is acidified with H_2SO_4. Barium carrier is added to precipitate barium sulfate and the sample is digested while warming up to 50°C for 30 minutes. Iron carrier is then added. After 30 minutes the sample is neutralized with dilute NH_4OH to precipitate ferric hydroxide. The sample is filtered and the precipitate is radioassayed after drying. This procedure precipitates radium and all alpha and beta emitting actinide elements.

Special Apparatus

1. Drying lamp.
2. Filter membranes, 47 mm dia., 0.45 micrometer pore size.
3. Glassware.
4. Magnetic stirrer and stirring bars.
5. Planchets, stainless steel, 5 cm diameter.
6. Low background internal proportional alpha counter.

Reagents

1. Ammonium hydroxide, 6$\underline{M}$. Dilute 400 ml reagent grade NH_4OH to 1 liter with distilled water.
2. Barium carrier, 5 mg Ba^{+2}/ml. Dissolve 4.4 g $BaCl_2 \bullet 2H_2O$ in 500 ml distilled water.
3. Bromocresol purple, 0.1 percent. Dissolve 100 mg of the water soluble reagent in 100 ml distilled water.
4. Iron carrier, 5 mg Fe^{+3}/ml. Dissolve 17.5 g $Fe(NO_3)_3 \bullet 9H_2O$ in 200 ml distilled water containing 2 ml 16$\underline{M}$ HNO_3. Dilute to 500 ml.
5. Nitric acid, 16$\underline{M}$, 70 percent HNO_3 reagent.

6. Sulfuric acid, 1M. Dilute 55 ml of the 96 percent reagent grade H_2SO_4 to 1 liter with distilled water.

Procedure

1. Use a measured aliquot of water sample. If the sample is less than 500 ml, dilute to 500 ml with distilled water.
2. If the sample used is preserved with acid, neutralize to color change with 6M NH_4OH using 1 ml bromocresol purple.
3. Add 20 ml 1M H_2SO_4 and flush the radon from the sample by boiling for two minutes.
4. Allow the sample to stand for three hours for radon progeny to decay.
5. Place sample on a magnetic stirrer/heater and add 1 ml barium carrier.
6. Heat the sample to approximately 50°C with stirring for 30 minutes.
7. Add 1 ml iron carrier and 1 ml bromocresol purple reagent.
8. Continue stirring and add 6M NH_4OH dropwise to the sample until the indicator changes color.
9. Continue warming and stirring for another 30 minutes.
10. Filter sample through a membrane and wash precipitate with 25 ml distilled water.
11. Mount the filter membrane on a planchet using double stick tape.
12. Carefully dry the precipitate and count for alpha activity.
13. Prepare a reagent blank precipitate to determine reagent background.
14. Store samples in a desiccator or dry carefully under a heat lamp if recounted at a later date.

Calculations

Calculate the concentration, Z, of gross alpha in picocuries per liter as follows:

$$Z = \frac{C_1 - C_B}{(2.22)(E)(V)}$$

where

E = counter efficiency (see Note 1),
V = volume analyzed (liters),
2.22 = dpm/pCi,
C_1 = sample (counts per minute), and
C_B = reagent blank (counts per minute).

Calculate the lower limit of detection (LLD), as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(V)(T)}$$

where

C_B = reagent background, counts per minute,
T = counting time,
E = counter efficiency,
V = sample volume (liters), and
2.22 = dpm/pCi.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

Notes

1. Determine counter efficiency by coprecipitating standardized aliquots of alpha-emitting actinide solutions. As an example, a known quantity

of plutonium is added to a 500 ml volume of water. The plutonium is coprecipitated by using the procedure described, counted and the counting efficiency determined. Other alpha emitters such as uranium may also be used in the manner described. At least six determinations should be made with each standard used.

References

1. Krieger, H.L., and Whittaker, E.L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio (August 1980).

RADIOCHEMICAL DETERMINATION OF LEAD-210 AND POLONIUM-210 IN DRY INORGANIC AND BIOLOGICAL SAMPLES

Principle

Polonium-209 and bismuth-207 tracers and lanthanum carrier are added to a weighed aliquot of sample which has been dried at 100°C for 24 hours. The sample is solubilized by wet ashing. The radioelements are coprecipitated as hydroxide with NH_4OH. The hydroxide is redissolved in acid and the bismuth and polonium are spontaneously deposited on a clean copper disc.

The disc is beta counted for ^{210}Bi, gamma assayed by Ge(Li) for ^{207}Bi and radioassayed by alpha spectroscopy for ^{209}Po and ^{210}Po. The ^{210}Pb can be determined by measuring ingrowth of its decay daughter ^{210}Bi which has a half-life of 5 days.

Special Apparatus

1. Copper discs made from 0.6 mm thick copper sheet. Discs are 2.2 cm diameter with a 0.3 cm hole set 0.15 cm in from the edges. The discs are coated on one side with an acid-resistant paint.
2. Constant temperature bath maintained at 80°C. Glycerol is used as heat transfer fluid.
3. Teflon beakers. See Note 1.
4. Centrifuge.
5. Magnetic stirrer and stirring bars.
6. Glassware.
7. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detector, vacuum pump and chamber.

Reagents

1. Ascorbic acid, crystalline reagent.
2. Ammonium hydroxide, 15M, reagent grade NH_4OH.

3. Hydrochloric acid, 12M, 37 percent HCl reagent.
4. Hydrochloric acid, 6M. Dilute 500 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
5. Hydrofluoric acid, 29M, 48 percent HF reagent.
6. Lanthanum carrier, 10 mg La^{+3}/ml. Dissolve 7.8g high purity $La(NO_3)_3 \cdot 6H_2O$ in 250 ml distilled water.
7. Nitric acid, 16M, 70 percent HNO_3 reagent.
8. Bismuth-207 tracer solution. Approximately 10 pCi/ml.
9. Polonium-209 tracer solution. Approximately 1 pCi/ml.

Procedure

1. Add measured aliquot of Bi-207 and Po-209 tracers and 1 ml lanthanum carrier to weighed one gram aliquot of sample in a Teflon beaker.
2. Add 15 ml 29M HF and 10 ml 16M HNO_3 and evaporate to near dryness. Repeat this step.
3. Add three successive 10 ml volumes of 6M HCl. Evaporate to near dryness following each addition.
4. Take up sample in 40 ml 6M HCl and cover with watch glass while warming sample for 30 minutes.
5. Transfer dissolved sample to 250 ml centrifuge bottle.
6. Make sample basic with careful addition of 15M NH_4OH with stirring.
7. Allow sample to stand for 30 minutes and centrifuge after precipitate has formed.
8. Pour off supernate. Wash precipitate with 25 ml water. Centrifuge and pour off wash water.
9. Dissolve precipitate by adding 1-ml increments of 12M HCl. Use stirring rod to break up precipitate, using minimum amount of HCl.
10. Place small magnetic stirring bar in centrifuge bottle and slowly add 100 ml water with stirring.

11. Transfer centrifuge bottle to constant temperature bath maintained at 80°C.
12. If yellow color is evident, add ascorbic acid in 50-mg increments until Fe^{+3} color is gone.
13. Prepare copper disc by cleaning bare side with copper cleaner and dipping disc in 12M HCl.
14. Suspend disc, using glass rod, into centrifuge bottle, keeping disc under surface of liquid.
15. Maintain sample at bath temperature of 80°C for four hours.
16. Remove disc, rinse with water and air dry.
17. Mount on 32 mm planchet with double stick tape for radioassay.

Appendix

Preparation of Bismuth-207 Standard Solution

Bismuth-207 decays by electron capture to lead-207m, which emits a gamma ray at 570 keV.

1. Evaporate a measured aliquot of the ^{207}Bi standard solution on a copper disc.
2. Radioassay the disc with a Ge(Li) detector for 1,000 minutes and record the net counts appearing under the 570 keV peak.
3. Radioassay the disc for beta activity using a beta counter having a window of 7 mg/cm^2 thickness. This assay determines the contribution to the beta background from the bismuth-207 added to the sample.

Calculations

Calculate the concentration, Z, of lead-210, bismuth-210 in picocuries per sample as follows:

$$Z = \frac{C_1 - [C_B + (C_{Bi} \cdot R)]}{(2.22)(R)(E)(V)(e^{-\lambda t})}$$

where

C_1 = sample beta counts per minute,
C_B = beta background, counts per minute,
C_{Bi} = beta counts of bismuth-207 aliquot added to sample,
R = chemical yield based on Ge(Li) counts of sample vs Ge(Li) counts of aliquot added to sample,
E = counter efficiency (7 mg/cm^2 window),
λ = decay constant for bismuth-210, $minutes^{-1}$,
t = time from separation to counting in minutes, using midpoints of intervals, and
V = sample unit (liters or grams).

Calculate the concentration, Z, of polonium-210 in picocuries per unit sample as follows:

$$Z = \frac{(A-A_1) \times F \ e^{-\lambda t}}{(2.22\ (B-B_1)(E)(V)(T)}$$

where

A = gross sample counts which appear in the polonium-210 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer counts which appear in the alpha energy region of the tracer isotope,
B_1 = background counts in the same alpha energy region as B above,
E = alpha detector efficiency,
F = total calibrated tracer counts for same counting time as sample counts,
λ = decay constant for polonium-210, days^{-1},
t = time from separation to counting in days,
V = sample unit (liters or grams),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) for bismuth or polonium in picocuries per unit sample as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(V)(T)}$$

where

C_B = background count rate,

T = counting time (same for sample and background),
E = alpha detector efficiency,
R = fractional yield based on $B-B_1/F$ in calculation, for Po (see R, ^{210}Bi calculation for Bi),
V = sample unit (liters or grams), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

Notes

1. Teflon is a registered tradmark of the DuPont Co., Wilmington, DE.

References

1. Blanchard, R. L., "Rapid Determination of Lead-210 and Polonium-210 in Environmental Samples by Deposition on Nickel," Analytical Chemistry, 38, 189 (1966).

RADIOCHEMICAL DETERMINATION OF PLUTONIUM, THORIUM AND URANIUM IN AIR FILTERS

Principle

The cellulose air filters are ashed at 550°C for 48 hours. Plutonium-242, thorium-234, and uranium-232 tracers are added to determine chemical yield. Silica is volatilized with HF and the residue is solubilized. Plutonium and uranium are extracted into triisooctylamine (TIOA). The thorium is purified by adsorption on anion exchange resin from nitric acid. Plutonium and uranium are stripped from the TIOA with dilute nitric acid and selectively coprecipitated with 0.1 mg lanthanum as fluoride. The precipitates are filtered on filter membranes and radioassayed by alpha spectroscopy for plutonium and uranium.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Ion exchange column, 2 cm I.D. x 10 cm.
3. Plastic graduated cylinder, 100 ml volume.
4. Planchets, stainless steel, 32 mm diameter.
5. Separatory funnels, 1 liter capacity.
6. Suction filter for 25 mm membrane.
7. Teflon beakers. See Note 2.
8. Glassware.
9. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump and chamber.

Reagents

1. Anion exchange resin; BioRad AG1X8 (200-400 mesh, nitrate form) or equivalent. Convert to nitrate form for thorium analysis by washing the resin with 6M HNO_3 until the washing shows no trace

of chloride, when tested with $AgNO_3$.

2. Ascorbic acid, crystalline reagent.
3. Ethanol, 95 percent reagent.
4. Hydrochloric acid, 12M. 37 percent HCl reagent.
5. Hydrochloric acid, 9M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
7. Hydrofluoric acid, 29M, 48 percent HF reagent.
8. Hydrofluoric acid, 3M,. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduate and storage bottle.
9. Hydrogen peroxide, 50 percent reagent grade.
10. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1M HCl.
11. Nickel foil, 15 cm x 1 cm x 0.1 mm.
12. Nitric acid, 16M, 70 percent HNO_3 reagent.
13. Nitric acid, 6M. Dilute 375 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
14. Nitric acid, 0.1M. Dilute 6 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
15. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
16. Silver nitrate, crystalline reagent.
17. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Add 1 ml 6M HNO_3 and dilute to 100 ml with distilled water.
18. Titanium trichloride, 20 percent reagent grade.
19. Titanium trichloride, 0.4 percent. Dilute 1 ml of the 20 percent $TiCl_3$ to 50 ml with 1 M HCl. Prepare fresh daily.
20. Triisooctylamine (TIOA), reagent grade.
21. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml of triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.

22. p-Xylene, reagent grade.
23. Thorium-234 tracer solution, approximately 800 pCi/ml, accurately calibrated.
24. Uranium-232 tracer solution, approximately 1 pCi/ml, accurately calibrated.
25. Plutonium-242 tracer solution, approximately 1 pCi/ml, accurately calibrated.

Sample Preparation

1. Place air filter samples in a ceramic dish for ashing.
2. Ash in muffle furnace, gradually raising temperature over several hours to 550°C. Maintain temperature for 48 hours.
3. Carefully weigh cooled ash and transfer to Teflon beaker. Add 1 ml each of ^{242}Pu, ^{234}Th, and ^{232}U tracers.
4. Add 20 ml of 29M HF and evaporate to dryness to remove SiF_4. Repeat.
5. Dissolve the residue in 200 ml 9M HCl and transfer solution to a separatory funnel.
6. Wash beaker with 25 ml 9M HCl and add solution to separatory funnel.
7. Add 2 ml of 50 percent H_2O_2, heat gently and set aside for 10 minutes. See Note 3.

Plutonium Determination

1. Place 100 ml of 10 percent TIOA solution in a 1 liter separatory funnel. Add 50 ml 9M HCl and shake funnel for one minute. Drain and discard lower aqueous acid phase after clean separation of the two phases.
2. Add the aqueous sample to the TIOA in the separatory funnel and shake the funnel vigorously for two minutes. Vent the funnel stopcock to prevent pressure buildup in the funnel.

3. Allow the phases to separate cleanly and draw off the lower aqueous acid phase. Save acid phase for thorium determination.
4. Add 50 ml 9M HCl to the TIOA solution in the separatory funnel and shake for one minute.
5. Allow the phases to separate; withdraw and discard lower aqueous acid phase.
6. Repeat steps 4 and 5.
7. Strip the plutonium from the TIOA solution by adding 100 ml 0.1M HNO_3 to the separatory funnel and shaking the funnel for two minutes.
8. Allow phases to separate; withdraw and transfer lower acid phase to separatory funnel.
9. Repeat steps 7 and 8 and combine strip solutions. Discard TIOA.
10. Place combined strip solutions in a separatory funnel.
11. Add 100 ml p-xylene to combined strip solution and shake funnel for one minute. See Note 4.
12. Allow phases to separate cleanly; withdraw lower aqueous acid layer into beaker. Discard p-xylene.
13. Evaporate combined solution from step 12 to dryness. Do not overheat.
14. Add 10 ml 16M HNO_3 to residue and evaporate to dryness. Do not overheat.
15. Add 5 ml 9M HCl and 5 ml 12M $HClO_4$ to residue and evaporate to dryness.
16. Repeat step 15.
17. Add 10 ml 12M HCl and evaporate to dryness.
18. Repeat step 17.
19. Add 50 ml 1M HCl to sample residue and warm gently to dissolve residue.
20. Heat sample solution to 80°C with stirring and add 50 mg ascorbic acid. Do not overheat.

21. Suspend clean nickel metal strip into solution for two hours to remove polonium.
22. Remove nickel and evaporate the solution to dryness.
23. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
24. Add 0.5 ml 50 percent H_2O_2, 1 ml of lanthanum carrier and 5 ml of 3M HF to precipitate LaF_3. Mix well and set aside for 30 minutes.
25. Using suction, filter coprecipitated sample through a filter membrane. Save filtrate for uranium analyses.
26. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
27. Remove clamp and top of funnel with suction on. Allow membrane to dry.
28. Mount membrane carefully on 32 mm planchet using double stick tape.
29. Count sample for 1000 minutes on alpha spectrometer.

Uranium Determination

1. Evaporate filtrate from step 25 of the plutonium determination.
2. Add 10 ml 12M HCl to residue and evaporate to dryness. Repeat this step.
3. Add 15 ml 1M HCl to sample residue and warm to approximately 50° C.
4. Add enough ascorbic acid to reduce iron in the sample, indicated by the disappearance of yellow color.
5. Add 1 ml of 0.4 percent $TiCl_3$ to reduce uranium.
6. Add 1 ml of lanthanum carrier and 5 ml of 3 M HF. Mix well and set aside for 30 minutes.
7. Using suction, filter coprecipitated sample through a filter membrane.
8. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.

9. Remove clamp and top of funnel with suction on. Allow membrane to dry.
10. Mount membrane carefully on 32 mm planchet using double stick tape.
11. Count sample for 1000 minutes on alpha spectrometer.

Thorium Determination

1. Evaporate aqueous acid fraction containing thorium from step 3 of plutonium determination.
2. Add 10 ml 16M HNO_3 and evaporate to dryness.
3. Add 5 ml 9M HCl and 5 ml 12M $HClO_4$ and evaporate to dryness.
4. Add 10 ml of 16M HNO_3 and evaporate to dryness.
5. Repeat step 4.
6. Dissolve sample in 10 ml of 6M HNO_3 with heat.
7. Prepare ion exchange column with 25 ml BioRad AG1X8 resin. Wash resin with 250 ml of 6M HNO_3.
8. Decant sample into column at gravity flow (approx. 3ml/min) and rinse the sample on the column with an additional 50 ml of 6M HNO_3. Discard wash.
9. Elute the thorium from the column with 200 ml of 6M HCl at flow rate of 3 ml/minute.
10. Evaporate thorium eluate to dryness.
11. Wet ash residue with 10 ml 12M HCl and evaporate to dryness.
12. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
13. Add 1 ml lanthanum carrier and 5 ml of 3M HF to precipitate LaF_3. Mix well and set aside for 30 minutes.
14. Using suction, filter coprecipitated sample through a filter membrane.
15. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
16. Remove clamp and top of funnel with suction on. Allow membrane to dry.

17. Mount membrane carefully on 32 mm planchet using double stick tape.
18. Beta count the sample to measure thorium-234 recovery.
19. Count sample for 1000 minutes on alpha spectrometer.

Calculations

Calculate the concentration, Z, of plutonium in picocuries per cubic meter as follows:

$$Z = \frac{(A-A_1) \times F}{(2.22)(B-B_1)(E)(V)(T)}$$

where

A = gross sample counts which appear in the plutonium-238 or plutonium-239 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer counts which appear in the alpha energy region of the tracer isotope,
B_1 = background counts in the same alpha energy region as B above,
E = alpha detector efficiency,
F = total calibrated tracer counts for same counting time as sample counts,
V = sample volume (cubic meters of air),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the concentration, Z, of uranium in picocuries per cubic meter as follows:

$$Z = \frac{(A-A_1) \times F}{(2.22)(B-B_1)(E)(V)(T)}$$

where

A = gross sample counts which appear in the uranium-234,-235, or-238 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer counts which appear in the alpha energy region of the tracer isotope,
B_1 = background counts in the same alpha energy region as B above.
E = alpha detector efficiency,
F = total calibrated tracer counts for same counting time as sample counts,
V = sample volume (cubic meters of air),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the concentration, Z, of thorium in picocuries per cubic meter as follows:

$$Z = \frac{(A - A_1) \times F}{(2.22)(B - B_1)(E)(V)(T)}$$

where

A = gross sample counts which appear in the thorium -227, -228, -230 or -232 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer beta counts,
B_1 = beta counter background,
E = alpha detector efficiency,
F = total calibrated tracer beta counts,
V = sample volume (cubic meters of air),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) in picocuries per cubic meter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(V)(T)}$$

where

C_B = background count rate,
T = counting time (same for sample and background),
E = alpha detector efficiency,
R = fractional yield based on $B-B_1/F$ in calculation,
V = sample volume (cubic meters of air), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.
2. Teflon is a registered trademark of Dupont Co., Wilmington, DE.
3. Hydrogen peroxide stabilizes the +4 plutonium valence necessary for maximum extraction into the TIOA.
4. The p-xylene removes most of the TIOA carried into the aqueous acid phase. Residual TIOA makes the coprecipitation step more difficult.

References

1. Moore, F.L., "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric Acid Solution with Tri(iso-octyl)amine," Analytical Chemistry 30, 908 (1958).

2. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.
3. Johns, F.B., et al., Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0539-17, U.S. E.P.A., Las Vegas, NV.

RADIOCHEMICAL DETERMINATION OF THORIUM AND URANIUM IN ASHED SAMPLES INCLUDING SOIL, COAL, FLY ASH, ORES, VEGETATION AND BIOTA

Fusion Method

Principle

The sample is ashed at 550°C for 72 hours. Thorium-234 and uranium-232 tracers are added to a weighed aliquot. Silica is volatilized and the sample is fused with potassium fluoride and potassium pyrosulfate. The uranium is extracted into triisooctylamine (TIOA). The thorium is purified by adsorption on anion exchange resin from nitric acid. Uranium is stripped from the resin with HCl and coprecipitated. Each actinide isotope is radioassayed by alpha spectroscopy.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Ion exchange column, 2 cm I.D. x 10 cm.
3. Plastic graduated cylinder, 100 ml capacity.
4. Planchets, stainless steel, 32 mm diameter.
5. Separatory funnels, 1 liter capacity.
6. Suction filter for 25 mm membrane.
7. Teflon beakers. See Note 2.
8. Glassware.
9. Platinum Crucible.
10. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detector, vacuum pump and chamber.
11. Meker burner.

Reagents

1. Anion exchange resin; BioRad AG1X8 (200-400 mesh, nitrate form)

or equivalent. Convert to nitrate form for thorium analysis by washing the resin with 6M HNO_3 until the washing shows no trace of chloride, when tested with $AgNO_3$.

2. Ascorbic acid, crystalline reagent.
3. Hydrochloric acid, 12M. 37 percent HCl reagent.
4. Hydrochloric acid, 9M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
5. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrofluoric acid, 29M, 48 percent HF reagent.
7. Hydrofluoric acid, 3M,. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduate and storage bottle.
8. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1M HCl.
9. Nickel foil, 15 cm x 1 cm x 0.1 mm.
10. Nitric acid, 16M, 70 percent HNO_3 reagent.
11. Nitric acid, 6M. Dilute 375 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
12. Nitric acid, 0.1M. Dilute 6 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
13. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
14. Potassium fluoride, crystalline reagent.
15. Potassium pyrosulfate, crystalline reagent.
16. Silver nitrate, crystalline reagent.
17. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Add 1 ml 6M HNO_3 and dilute to 100 ml with distilled water. Keep in brown bottle.
18. Sulfuric acid, 3M. Dilute 167 ml of the 96 percent H_2SO_4 reagent to 1 liter with distilled water.
19. Titanium trichloride, 20 percent reagent grade.

20. Titanium trichloride, 0.4 percent. Dilute 1 ml of the 20 percent $TiCl_3$ to 50 ml with 1 M HCl. Prepare fresh daily.
21. Triisooctylamine (TIOA), reagent grade.
22. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml of triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
23. p-Xylene, reagent grade.
24. Thorium-234 tracer solution, approximately 800 pCi/ml, accurately calibrated.
25. Uranium-232 tracer solution, approximately 1 pCi/ml, accurately calibrated.

Sample Preparation

1. Place 100 g sample in ceramic dish for ashing.
2. Ash in muffle furnace, gradually raising temperature over several hours to 550°C. Maintain at temperature for 72 hours.
3. Carefully weigh 1 g aliquot of cooled ash and transfer to Teflon beaker. Add 1 ml each of ^{234}Th and ^{232}U tracers.
4. Wet ash with two additions of 20 ml each 29M HF and evaporate each time to dryness.
5. Transfer the residue to a platinum crucible with the aid of a spatula. Use a 20 ml crucible for a 1 g sample.
6. Add 2g of KF for a 1g sample or 4g KF for a 5g sample and fuse covered over a Meker burner for 30 minutes.
7. Add 7.5 grams $K_2S_2O_7$ for a 5-gram sample or 3 grams for a 1-gram sample and continue fusing for 30 minutes.
8. Cool the crucible in an ice bath, add 15 ml 12M HCl and evaporate.
9. Add 15 ml of water and partially evaporate to 10 ml volume.
10. Transfer to 1000-ml beaker and add 150 ml water.
11. Heat and evaporate to dryness and add 200 ml 3M H_2SO_4. Evaporate past white fumes to dryness.
12. Dissolve the residue in 200 ml 9M HCl.

Uranium Determination

1. Place 100 ml of 10 percent TIOA solution in a 1 liter separatory funnel. Add 50 ml 9M HCl and shake funnel for 1 minute. Drain and discard lower aqueous acid phase after clean separation of the two phases.
2. Add the aqueous sample from step 12 above, to the TIOA in the separatory funnel and shake the funnel vigorously for two minutes. Vent the funnel stopcock to prevent pressure buildup in the funnel.
3. Allow the phases to separate cleanly and draw off the lower aqueous acid phase. Save for thorium analysis.
4. Add 50 ml 9M HCl to the TIOA solution in the separatory funnel and shake for 1 minute.
5. Allow the phases to separate; withdraw and discard lower aqueous acid phase.
6. Repeat steps 4 and 5.
7. Strip the uranium from the TIOA solution by adding 100 ml 0.1 M HNO_3 to the separatory funnel and shaking the funnel for 2 minutes.
8. Allow phases to separate; withdraw and save lower acid phase, discard organic phase.
9. Repeat steps 7 and 8 and combine strip solutions.
10. Place combined strip solutions in the clean separatory funnel.
11. Add 100 ml p-xylene to combined strip solution and shake funnel for 1 minute. See Note 3.
12. Allow phases to separate cleanly; withdraw lower aqueous acid layer into beaker.
13. Evaporate combined solution from step 12 to dryness. Discard organic phase. Do not overheat.
14. Add 100 ml 16M HNO_3 to residue and evaporate to dryness. Do not overheat.

15. Add 5 ml 9M HCl and 5 ml 12M $HClO_4$ to residue and evaporate to dryness.
16. Repeat step 15.
17. Add 10 ml 12M HCl and evaporate to dryness.
18. Repeat step 17.
19. Add 50 ml 1M HCl to sample residue and warm gently to dissolve residue.
20. Heat sample solution to 80°C with stirring and add 50 mg ascorbic acid. Do not overheat.
21. Suspend clean nickel metal strip into solution for two hours to remove polonium.
22. Remove nickel and evaporate solution to dryness.
23. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
24. Add enough ascorbic acid to reduce iron in the sample, indicated by the disappearance of yellow color.
25. Add 1 ml of 0.4 percent $TiCl_3$ to reduce uranium.
26. Add 1 ml of lanthanum carrier and 5 ml of 3M HF. Mix well and set aside for 30 minutes.
27. Using suction, filter coprecipitated sample through a filter membrane.
28. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
29. Remove clamp and top of funnel with suction on. Allow membrane to dry.
30. Mount membrane carefully on 32 mm planchet using double stick tape.
31. Count sample for 1000 minutes on alpha spectrometer.

Thorium Determination

1. Evaporate aqueous acid fraction containing thorium from step 3 of Uranium Determination.
2. Add 10 ml 16M HNO_3 and evaporate to dryness.

3. Add 5 ml 9M HCl and 5 ml 12M $HClO_4$ and evaporate to dryness.
4. Add 10 ml of 16M HNO_3 and evaporate to dryness.
5. Repeat step 4.
6. Dissolve sample in 10 ml of 6M HNO_3 with heat.
7. Prepare ion exchange column with 25 ml BioRad AG1X8 resin. Wash resin with 250 ml of 6M HNO_3.
8. Decant sample into column at gravity flow (approx. 3ml/min) and rinse the sample on the column with an additional 50 ml of 6M HNO_3. Discard wash.
9. Elute the thorium from the column with 200 ml of 6M HCl at flow rate of 3 ml/minute.
10. Evaporate thorium eluate to dryness.
11. Add 10 ml 12M HCl to residue and evaporate to dryness.
12. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
13. Add 1 ml lanthanum carrier and 5 ml of 3M HF. Mix well and set aside for 30 minutes.
14. Using suction, filter coprecipitated sample through a filter membrane.
15. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
16. Remove clamp and top of funnel with suction on. Allow membrane to dry.
17. Mount membrane carefully on 32 mm planchet using double stick tape.
18. Beta count the sample to measure thorium-234 recovery.
19. Count sample for 1000 minutes on alpha spectrometer.

Calculations

Calculate the concentration, Z, of uranium in picocuries per gram as follows:

$$Z = \frac{(A-A_1) \times F}{(2.22)(B-B_1)(E)(W)(T)}$$

where

A = gross sample counts which appear in the uranium-234,-235, or-238 alpha energy region,

A_1 = background counts in the same alpha energy region as A above,

B = gross tracer counts which appear in the alpha energy region of the tracer isotope,

B_1 = background counts in the same alpha energy region as B above,

E = alpha detector efficiency,

F = total calibrated tracer counts for same counting time as sample counts,

W = sample weight (grams),

T = counting time (minutes), and

2.22 = dpm per pCi.

Calculate the concentration, Z, of thorium in picocuries per gram as follows:

$$Z = \frac{(A - A_1) \times F}{(2.22)(B - B_1)(E)(W)(T)}$$

where

A = gross sample counts which appear in the thorium -227, -228, -230 or -232 alpha energy region,

A_1 = background counts in the same alpha energy region as A above,

B = gross tracer beta counts,

B_1 = beta counter background,

E = alpha detector efficiency,

F = total calibrated tracer beta counts,

W = sample weight (grams),

T = counting time (minutes), and

2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) for uranium or thorium in picocuries per gram as follows:

$$\text{LLD} = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(W)(T)}$$

where

C_B = background count rate,
T = counting time; same for sample and background,
E = alpha detector efficiency,
R = fractional yield based on $B\text{-}B_1/F$ in calculation,
W = sample weight (grams), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is the same as the background counting time.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.
2. Teflon is a registered trademark of Dupont, Co., Wilmington, DE.
3. The p-xylene removes most of the TIOA carried into the aqueous acid phase. Residual TIOA makes the coprecipitation step more difficult.

References

1. Moore, F.L., "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric acid Solution with Tri (iso-octyl) amine," Analytical Chemistry 30, 908 (1958).
2. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.
3. Johns, F.B., et al., Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0539-17, U.S. E.P.A., Las Vegas, NV, (1979).

RADIOCHEMICAL DETERMINATION OF THORIUM AND URANIUM IN ASHED SAMPLES

Nonfusion Method

Principle

The sample is ashed at 550°C for 72 hours. Thorium-234 and uranium-232 tracers are added to 1 g aliquots. Silica is volatilized with HF and the residue is solubilized. The uranium is extracted into triisooctylamine (TIOA), stripped from the TIOA with nitric acid and coprecipitated. The thorium is purified by adsorption on anion exchange resin from nitric acid, stripped from the resin with HCl and coprecipitated. Each isotope is radioassayed by alpha spectroscopy.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Ion exchange column, 2 cm internal diameter x 10 cm.
3. Plastic graduated cylinder.
4. Planchets, stainless steel, 32 mm diameter.
5. Separatory funnels, 1 liter capacity.
6. Suction filter for 25 mm membrane.
7. Teflon beakers. See Note 2.
8. Glassware.
9. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump and chamber.

Reagents

1. Anion exchange resin; BioRad AG1X8 (200-400 mesh, nitrate form) or equivalent. Convert to nitrate form for thorium analysis by washing the resin with 6M HNO_3 until the washing shows no trace of chloride when tested with $AgNO_3$.

2. Ascorbic acid, crystalline reagent.
3. Hydrochloric acid, 12M. 37 percent HCl reagent.
4. Hydrochloric acid, 9M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
5. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrofluoric acid, 29M, 48 percent HF reagent.
7. Hydrofluoric acid, 3M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduated cylinder and storage bottle.
8. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g $La(NO_3)_3 \bullet 6H_2O$ per 250 ml 1M HCl.
9. Nickel foil, 15 cm x 1 cm x 0.1 mm.
10. Nitric acid, 16M, 70 percent HNO_3 reagent.
11. Nitric acid, 6M. Dilute 375 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
12. Nitric acid, 0.1M. Dilute 6 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
13. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
14. Silver nitrate, crystalline reagent.
15. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Add 1 ml 6M HNO_3 and dilute to 100 ml with distilled water.
16. Titanium trichloride, 20 percent reagent grade.
17. Titanium trichloride, 0.4 percent. Dilute 1 ml of the 20 percent $TiCl_3$ to 50 ml with 1 M HCl. Prepare fresh daily.
18. Triisooctylamine (TIOA), reagent grade.
19. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml of triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
20. p-Xylene, reagent grade.
21. Thorium-234 tracer solution, approximately 800 pCi/ml, accurately calibrated.

22. Uranium-232 tracer solution, approximately 1 pCi/ml, accurately calibrated.

Sample Preparation

1. Place 100g sample in ceramic dish for ashing.
2. Ash in muffle furnace, gradually raising temperature over several hours to 550°C. Maintain temperature for 72 hours.
3. Carefully weigh 1g aliquot of cooled ash and transfer to Teflon beaker. Add 1 ml each of ^{234}Th and ^{232}U tracers.
4. Treat sample with two additions of 20 ml each 29M HF and evaporate each time to dryness.

Uranium Determination

1. Add 5 ml of 12M $HClO_4$ and 5 ml of 9M HCl to sample and evaporate to dryness. Repeat this step.
2. Add 10 ml of 12M HCl and transfer sample to glass beaker. Evaporate to dryness and repeat this step.
3. Dissolve sample in 300 ml of 9M HCl and warm to approximately 50°C.
4. Place 100 ml of 10 percent TIOA solution in a 1 liter separatory funnel. Add 50 ml 9M HCl and shake funnel for 1 minute. Drain and discard lower aqueous acid phase after clean separation of the two phases.
5. Add the aqueous sample to the TIOA in the separatory funnel and shake the funnel vigorously for two minutes. Vent the funnel stopcock to prevent pressure buildup in the funnel.
6. Allow the phases to separate cleanly and draw off the lower aqueous acid phase. Save for thorium analysis.
7. Add 50 ml 9M HCl to the TIOA solution in the separatory funnel and shake for one minute.
8. Allow the phases to separate; withdraw and discard lower aqueous acid phase.

9. Repeat steps 7 and 8.
10. Strip the uranium from the TIOA solution by adding 100 ml 0.1 M HNO_3 to the separatory funnel and shaking the funnel for two minutes.
11. Allow phases to separate; withdraw and save lower acid phase.
12. Repeat steps 10 and 11 and combine strip solutions.
13. Place combined strip solutions in clean separatory funnel.
14. Add 100 ml p-xylene to combined strip solution and shake funnel for 1 minute. See Note 3.
15. Allow phases to separate cleanly; withdraw lower aqueous acid layer into beaker. Discard p-xylene.
16. Evaporate solution from step 15 to dryness. Do not overheat.
17. Add 100 ml 16M HNO_3 to residue and evaporate to dryness. Do not overheat.
18. Add 5 ml 9M HCl and 5ml 12M $HClO_4$ to residue and evaporate to dryness.
19. Repeat step 18.
20. Add 10 ml 12M HCl and evaporate to dryness.
21. Repeat step 20.
22. Add 50 ml 1M HCl to sample residue and warm gently to dissolve residue.
23. Heat sample solution to 80°C with stirring and add 50 mg ascorbic acid. Do not overheat.
24. Suspend clean nickel metal strip into solution for two hours to remove polonium.
25. Remove nickel and evaporate solution to dryness.
26. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
27. Add enough ascorbic acid to reduce iron in the sample, indicated by the disappearance of yellow color.
28. Add 1 ml of 0.4 percent $TiCl_3$ to reduce uranium.
29. Add 1 ml of lanthanum carrier and 5 ml of 3 M HF. Mix well and set aside for 30 minutes to precipitate LaF_3 carrying uranium.

30. Using suction, filter coprecipitated sample through a filter membrane.
31. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
32. Remove clamp and top of funnel with suction on. Allow membrane to dry.
33. Mount membrane carefully on 32 mm planchet using double stick tape.
34. Count sample for 1000 minutes on alpha spectrometer.

Thorium Determination

1. Evaporate aqueous acid fraction containing thorium from step 6 of Uranium Determination.
2. Add 10 ml 16M HNO_3 and evaporate to dryness.
3. Add 5 ml 9M HCl and 5 ml 12M $HClO_4$ and evaporate to dryness.
4. Add 10 ml of 16M HNO_3 and evaporate to dryness.
5. Repeat step 4.
6. Dissolve sample in 10 ml of 6M HNO_3 with heat.
7. Prepare ion exchange column with 25 ml BioRad AG1X8 resin. Wash resin with 250 ml of 6M HNO_3.
8. Decant sample into column at gravity flow (approx. 3ml/min) and rinse the sample on the column with an additional 50 ml of 6M HNO_3. Discard wash.
9. Elute the thorium from the column with 200 ml of 6M HCl at flow rate of 3 ml/minute.
10. Evaporate thorium eluate to dryness.
11. Add 10 ml 12M HCl to residue and evaporate to dryness.
12. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
13. Add 1 ml lanthanum carrier and 5 ml of 3M HF. Mix well and set aside for 30 minutes to precipitate LaF_3 carrying thorium.
14. Using suction, filter coprecipitated sample through a filter membrane.

15. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
16. Remove clamp and top of funnel with suction on. Allow membrane to dry.
17. Mount membrane carefully on 32 mm planchet using double stick tape.
18. Beta count the sample to measure thorium-234 recovery.
19. Count sample for 1000 minutes on alpha spectrometer.

Calculations

Calculate the concentration, Z, of uranium in picocuries per gram as follows:

$$Z = \frac{(A-A_1) \times F}{(2.22)(B-B_1)(E)(W)(T)}$$

where

A = gross sample counts which appear in the uranium-234,-235, or-238 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer counts which appear in the alpha energy region of the tracer isotope,
B_1 = background counts in the same alpha energy region as B above,
E = alpha detector efficiency,
F = total calibrated tracer counts for same counting time as sample counts,
W = sample weight (grams),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the concentration, Z, of thorium in picocuries per gram as follows:

$$Z = \frac{(A - A_1) \times F}{(2.22)(B - B_1)(E)(W)(T)}$$

where

A = gross sample counts which appear in the thorium -227, -228, -230 or -232 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer beta counts,
B_1 = beta counter background,
E = alpha detector efficiency,
F = total calibrated tracer beta counts,
W = sample weight (grams),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) of uranium or thorium in picocuries per gram as follows:

$$LLD = \frac{4.66 \sqrt{A_1 T}}{(2.22)(E)(R)(W)(T)}$$

where

A_1 = background counts in the same alpha energy region as A above,
T = counting time; same for sample and background,
E = alpha detector efficiency,
R = fractional yield based on $B-B_1/F$ in calculation,
W = sample weight (grams), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is same as the background counting time.

Notes

1. Nuclepore is a registered trademark of Nuclepore Corp., Pleasanton, CA.
2. Teflon is a registered trademark of Dupont, Co., Wilmington, DE.
3. The p-xylene removes most of the TIOA carried into the aqueous acid phase. Residual TIOA makes the coprecipitation step more difficult.

References

1. Moore, F.L., "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric acid Solution with Tri (iso-octyl) amine," Analytical Chemistry 30, 908 (1958).
2. Volchok, H. L. and dePlanque, G., editors, EML Procedures Manual, 25th Ed., Environmental Measurement Laboratory, U.S. Department of Energy, New York.
3. Johns, F.B., et al., Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0539-17, U.S. E.P.A., Las Vegas, NV, (1979).

RADIOCHEMICAL DETERMINATION OF THORIUM AND URANIUM IN WATER

Principle

The water sample is filtered. Thorium-234 and uranium-232 tracers are added to 1 to 4 liter aliquots. After evaporation, the uranium is extracted into triisooctylamine (TIOA). The thorium is purified by adsorption on anion exchange resin from nitric acid. Uranium is stripped from the TIOA with nitric acid and coprecipitated. Thorium is stripped from the resin with HCl and coprecipitated. Each actinide is radioassayed by alpha spectroscopy.

Special Apparatus

1. Nuclepore filter membranes, 25 mm dia., 0.2 micrometer pore size or equivalent. See Note 1.
2. Ion exchange column, 2 cm internal diameter x 10 cm.
3. Plastic graduated cylinder, 100 ml volume.
4. Planchets, stainless steel, 32 mm diameter.
5. Separatory funnels, 1 liter capacity.
6. Suction filter for 25 mm membrane.
7. Teflon beakers. See Note 2.
8. Glassware.
9. Pleated filter paper.
10. Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump and chamber.

Reagents

1. Anion exchange resin; BioRad AG1X8 (200-400 mesh, nitrate form) or equivalent. Convert to nitrate form for thorium analysis by washing the resin with 6M HNO_3 until the washing shows no trace of chloride, when tested with $AgNO_3$.
2. Ascorbic acid, crystalline reagent.

3. Hydrochloric acid, 12M. 37 percent HCl reagent.
4. Hydrochloric acid, 9M. Dilute 750 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
5. Hydrochloric acid, 1M. Dilute 83 ml of the 37 percent reagent grade HCl to 1 liter with distilled water.
6. Hydrofluoric acid, 29M, 48 percent HF reagent.
7. Hydrofluoric acid, 3M. Dilute 104 ml of the 48 percent reagent grade HF to 1 liter with distilled water. Use a plastic graduated cylinder and storage bottle.
8. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1M HCl.
9. Nickel foil, 15 cm x 1 cm x 0.1 mm.
10. Nitric acid, 16M, 70 percent HNO_3 reagent.
11. Nitric acid, 6M. Dilute 375 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
12. Nitric acid, 0.1M. Dilute 6 ml of the 70 percent reagent grade HNO_3 to 1 liter with distilled water.
13. Perchloric acid, 12M, 70 percent $HClO_4$ reagent.
14. Silver nitrate, crystalline reagent.
15. Silver nitrate, 0.1M. Dissolve 1.7 g $AgNO_3$ reagent in distilled water. Add 1 ml 6M HNO_3 and dilute to 100 ml with distilled water.
16. Titanium trichloride, 20 percent reagent grade.
17. Titanium trichloride, 0.4 percent. Dilute 1 ml of the 20 percent $TiCl_3$ to 50 ml with 1 M HCl. Prepare fresh daily.
18. Triisooctylamine (TIOA), reagent grade.
19. TIOA solution in p-xylene, 10 percent. Dissolve 100 ml of triisooctylamine in p-xylene and dilute to 1 liter with p-xylene.
20. p-Xylene, reagent grade.
21. Thorium-234 tracer solution, approximately 800 pCi/ml, accurately calibrated.
22. Uranium-232 tracer solution, approximately 1 pCi/ml, accurately calibrated.

Sample Preparation

1. Filter water sample of one to four liters through a pleated filter.
2. Add 50 ml 12M HCl and measured aliquots of ^{234}Th and ^{232}U tracers.
3. Evaporate sample to 200 ml volume.
4. Add 600 ml of 12M HCl to make sample concentration 9M in HCl.

Uranium Determination

1. Place 100 ml of 10 percent TIOA solution in a 1 liter separatory funnel. Add 50 ml 9M HCl and shake funnel for one minute. Drain and discard lower aqueous acid phase after clean separation of the two phases.
2. Add the aqueous acid sample to the TIOA in the separatory funnel and shake the funnel vigorously for two minutes. Vent the funnel stopcock to prevent pressure buildup in the funnel.
3. Allow the phases to separate cleanly and draw off the lower aqueous acid phase. Save for thorium analysis.
4. Add 50 ml 9M HCl to the TIOA solution in the separatory funnel and shake for one minute.
5. Allow the phases to separate; withdraw and discard lower aqueous acid phase.
6. Repeat steps 4 and 5.
7. Strip the uranium from the TIOA solution by adding 100 ml 0.1M HNO_3 to the separatory funnel and shaking the funnel for two minutes.
8. Allow phases to separate; withdraw and save lower acid phase.
9. Repeat steps 7 and 8 and combine strip solutions. Discard TIOA solution.
10. Place combined strip solutions in the clean separatory funnel.
11. Add 100 ml p-xylene to combined strip solution and shake funnel for one minute. See Note 3.

12. Allow phases to separate cleanly; withdraw lower aqueous acid layer into beaker. Discard p-xylene.
13. Evaporate combined solution from step 12 to dryness. Do not overheat.
14. Add 100 ml 16M HNO_3 to residue and evaporate to dryness. Do not overheat.
15. Add 5 ml 9M HCl and 5ml 12M $HClO_4$ to residue and evaporate to dryness.
16. Repeat step 15.
17. Add 10 ml 12M HCl and evaporate to dryness.
18. Repeat step 17.
19. Add 50 ml 1M HCl to sample residue and warm gently to dissolve residue.
20. Heat sample solution to 80°C with stirring and add 50 mg ascorbic acid. Do not overheat.
21. Suspend clean nickel metal strip into solution for two hours to remove polonium.
22. Remove nickel and evaporate solution to dryness.
23. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
24. Add enough ascorbic acid to reduce iron in the sample, indicated by the disappearance of yellow color.
25. Add 1 ml of 0.4 percent $TiCl_3$ to reduce uranium.
26. Add 1 ml of lanthanum carrier and 5 ml of 3M HF to precipitate LaF_3 carrying uranium. Mix well and set aside for 30 minutes.
27. Using suction, filter coprecipitated sample through a filter membrane.
28. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
29. Remove clamp and top of funnel with suction on. Allow membrane to dry.

30. Mount membrane carefully on 32 mm planchet using double stick tape.
31. Count sample for 1000 minutes on alpha spectrometer.

Thorium Determination

1. Evaporate aqueous acid fraction containing thorium from step 3 of Uranium Determination.
2. Add 10 ml 16M HNO_3 and evaporate to dryness.
3. Add 5 ml 9M HCl and 5 ml 12M $HClO_4$ and evaporate to dryness.
4. Add 10 ml of 16M HNO_3 and evaporate to dryness.
5. Repeat step 4.
6. Dissolve sample in 10 ml of 6M HNO_3 with heat.
7. Prepare ion exchange column with 25 ml BioRad AG1X8 resin. Wash resin with 250 ml of 6M HNO_3.
8. Decant sample into column at gravity flow (approx. 3ml/min) and rinse the sample on the column with an additional 50 ml of 6M HNO_3. Discard wash.
9. Elute the thorium from the column with 200 ml of 6M HCl at flow rate of 3 ml/minute.
10. Evaporate thorium eluate to dryness.
11. Add 10 ml 12M HCl to residue and evaporate to dryness.
12. Add 15 ml 1M HCl to sample residue and warm to approximately 50°C.
13. Add 1 ml lanthanum carrier and 5 ml of 3M HF. Mix well and set aside for 30 minutes.
14. Using suction, filter coprecipitated sample through a filter membrane.
15. Rinse sample beaker with 10 ml water and add to filter funnel. Rinse beaker with 10 ml ethanol and add to funnel.
16. Remove clamp and top of funnel with suction on. Allow membrane to dry.
17. Mount membrane carefully on 32 mm planchet using double stick tape.

18. Beta count the sample to measure thorium-234 recovery.
19. Count sample for 1000 minutes on alpha spectrometer.

Calculations

Calculate the concentration, Z, of uranium in picocuries per liter as follows:

$$Z = \frac{(A-A_1) \times F}{(2.22)(B-B_1)(E)(V)(T)}$$

where

A = gross sample counts which appear in the uranium-234,-235, or-238 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer counts which appear in the alpha energy region of the tracer isotope,
B_1 = background counts in the same alpha energy region as B above,
E = alpha detector efficiency,
F = total calibrated tracer counts for same counting time as sample counts,
V = sample volume (liters),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the concentration, Z, of thorium in picocuries per liter as follows:

$$Z = \frac{(A - A_1) \times F}{(2.22)(B - B_1)(E)(V)(T)}$$

where

A = gross sample counts which appear in the thorium -227, -228, -230 or -232 alpha energy region,
A_1 = background counts in the same alpha energy region as A above,
B = gross tracer beta counts,
B_1 = beta counter background,
E = alpha detector efficiency,
F = total calibrated tracer beta counts,
V = sample volume (liters),
T = counting time (minutes), and
2.22 = dpm per pCi.

Calculate the lower limit of detection (LLD) for thorium in picocuries per liter as follows:

$$LLD = \frac{4.66\sqrt{C_B T}}{(2.22)(E)(R)(W)(T)}$$

where

C_B = background count rate,
T = counting time (same for sample and background),
E = alpha detector efficiency,
R = fractional yield based on $B-B_1/F$ in calculation,
V = sample volume (liters), and
2.22 = dpm per pCi.

This LLD calculation is valid if the sample counting time is the same as the background counting time.

Notes

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2. Teflon is a registered trademark of Dupont, Co., Wilmington, DE.
3. The p-xylene removes most of the TIOA carried into the aqueous acid phase. Residual TIOA makes the coprecipitation step more difficult.

References

1. Moore, F.L., "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric acid Solution with Tri (iso-octyl) amine," Analytical Chemistry 30, 908 (1958).